

CONFERENCE PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE NO. 3

Constellation Hotel Toronto, Ontario

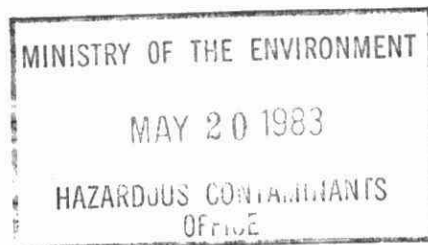
DECEMBER 7, 1982

RESEARCH ADVISORY COMMITTEE

Ministry of the Environment

Province of Ontario

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Constellation Hotel, Toronto, Ontario  
December 7, 1982

RESEARCH ADVISORY COMMITTEE  
Ministry of the Environment  
Province of Ontario

The Honourable Keith C. Norton  
Minister

Gerard J. M. Raymond  
Deputy Minister



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## INTRODUCTION

Ministry of the Environment  
Province of Ontario

Technology Transfer Conference No. 3  
December 7, 1982

Constellation Hotel  
900 Dixon Road  
Toronto, Ontario M9W 1J7

Featuring Completed Research Projects  
Supported by the  
Provincial Lottery Trust Fund

Sponsored and Presented by the  
Research Advisory Committee,  
Ministry of the Environment

The Research Advisory Committee, Ontario Ministry of the Environment, sponsored Technology Transfer Conference No. 3 on December 7, 1982 at the Constellation Hotel for the purpose of distributing information arising from Provincial Lottery Research Projects and from other selected M.O.E. in-house and external research projects. At this Conference, Contractors, Principal Investigators, Liaison Officers and Researchers described and discussed results of their projects giving emphasis to useful applications of the investigational work.

The attendance of approximately 180 people at this one-day session was divided between two parallel sessions of their choice. The program was structured for M.O.E. Staff and Researchers, Ontario and Federal Government Personnel, Consultants, Contractors, University Personnel, Industry Representatives and the Media.

Twenty-one papers were given at the Conference and, of these, eight were supported with Provincial Lottery Trust Funds. If information is required on any of these papers, it is suggested that the speakers be contacted at the addresses shown in the Table of Contents.

## ACKNOWLEDGEMENT

These Conference Proceedings are issued to describe environmental-oriented research projects conducted by the Ontario Government, assisted by the Federal Government, Universities and the Private Sector. All initial enquiries regarding the papers given at the Conference should be made to the authors and speakers or to their affiliation.

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### Session Chairmen at Conference No. 3

B. I. Boyko	Waste Management Branch
D. N. Jeffs	Water Resources Branch
D. A. McTavish	Southwestern Region
G. C. Ronan	Laboratory Services & Applied Research Branch

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CHARACTERIZATION & IDENTIFICATION OF  
ORGANIC SUBSTANCES IN DRINKING WATER

Bejoy S. Das and Gordon H. Thomas

Ontario Research Foundation  
Mississauga, Ontario

Ministry of the Environment Technology Transfer Conference No. 3  
December 7, 1982, at the Constellation Hotel, Toronto, Ontario

Abstract for Paper No. A1

The overall goal of the study was to develop methods for the isolation/characterization of organics from water and then apply the procedures in a water monitoring program. A combination of techniques were used in order to characterize three major categories of organic compounds which represent a wide spectrum of organic compounds found in drinking water. The three categories were volatile purgeable organics, semi-volatile priority pollutants and non-volatile polar high molecular weight compounds. A specific extraction and analytical technique was required for each category.

1. Volatile purgeable organics were determined using a Purge & Trap procedure.
2. An on-site XAD-2 resin accumulator column was used to collect non-polar organic compounds from tap water at the sampling sites. The collection method was used in order to provide a solution of organic compounds in the form of an extract in concentrations necessary for GC-FID-MS analysis. A clean-up procedure using high performance liquid chromatography with a nitrile-amino (Partisil PAC) column was developed to separate the polar humic/fulvic high molecular weight organics from the non-polar gas chromatographable organics in the accumulator column extracts. High resolution fused silica capillary chromatographic methods were developed for the separation and identification of the organic compounds in the accumulator column extracts. A total of 49 selected organic priority pollutants were utilized during the HR-GC development studies.

3. A combination of techniques developed at ORF were used to isolate and fractionate the non-volatile high MW organics from water. Fractionation studies were carried out by an adsorption/desorption technique on Amberlite XAD-2 and Ambersorb XE-340 resins in tandem. The extent of fractionation was monitored by TOC. The resin extract fractions were characterized by apparent molecular weight distribution (AMWD) determined using TSK  $\mu$ -Spherogel size exclusion high performance liquid chromatography.

Drinking water samples were collected for monitoring purposes at two water treatment plants. The results of the method development studies and their application during the monitoring phase of the program will be presented.



**OZONE AS AN ALTERNATE  
TO CHLORINE FOR DRINKING  
WATER DISINFECTION**

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## INTRODUCTION

The role of chlorination in drinking water disinfection is being re-examined as a result of the discovery of trihalomethanes in Dutch drinking water by Rook (1974). Subsequently, trihalomethanes were measured in North American drinking water by Bellar and Lichtenberg (1974), by Symons et al of the USEPA (1975), by Nicholson et al of the Ontario Ministry of the Environment (1976) and Health and Welfare Canada (1977). Ontario MOE data (1977) indicated that ten of forty-two municipalities had total trihalomethane levels in their drinking water in excess of 100 ug/L in the summer months, as measured by the direct aqueous injection (DAI) method.

Chloroform has been declared a potential carcinogen and bromo-chloro-methanes have been found to be mutagenic. This resulted in the promulgation of a 100 ug/L limit on total trihalomethanes in drinking waters by the U.S. EPA in the 29 November 1979 Federal Register. Alternate disinfectants such as ozone, chlorine dioxide, chloramine, ultraviolet and gamma irradiation are now being investigated to minimize the formation of these potentially hazardous compounds.

IEC has just completed a study for the Ontario Ministry of the Environment to investigate the technical feasibility and public health aspects of ozonation to reduce the concentrations of trihalomethanes in drinking water by replacing chlorine in the disinfection process. The project involved the use of both bench and pilot scale water treatment systems to evaluate ozone application for the primary or pre-disinfection step, and considered both chlorine and chloramine for the secondary or post-chlorination step. This paper presents the results of the three-year study funded under the Ontario Lottery Program, and presents recommendations for the application of ozone for water treatment.

## PROJECT DESCRIPTION

### Objectives

The specific objectives of this program were:

- to demonstrate the effectiveness of ozonation as a water treatment step for controlling the production of trihalomethanes and other chlorinated organics in water treatment.
- to investigate the practical methods which might be employed in water treatment plants to reduce the formation of undesirable by-products.
- to assess the add-on cost of providing ozonation at existing water treatment plants.
- to identify as many of the organic by-products of ozonation of surface water supplies as possible.
- to assess the public health effects of ozonation with respect to disinfection and mutagenic activity.

### Approach

The two-phased study described in this paper examined the feasibility of using ozone in Ontario for the treatment of drinking water supplies.

Phase I consisted of the following major tasks:

- literature review
- bench scale batch experiments on application of ozone followed by chlorine or chloramine
- mutagenicity assessment of the organic by-products of ozonation, ozonation/chlorination, and ozonation/chloramination
- identification of organic by-products by GC/MS and HPLC/UV fluorescence

Raw waters from three Ontario municipalities were used in the experimental work to evaluate the potential for both the formation and the minimization of trihalomethanes and other chlorinated organics in the disinfection process. Brantford and Lindsay were selected as they represented water supplies from an industrialized area, and rural area respectively, with high DOC. Toronto was also selected because it draws water from Lake Ontario which serves as a water supply for a large portion of Ontario's population and had a low DOC.

In Phase 2, the following major tasks were completed:

- literature review
- seasonal pilot-scale testing of ozone followed by chlorine or chloramine to confirm the results of Phase 1 under field conditions
- preparation of cost estimates for providing add-on ozonation at existing water treatment plants.

The pilot plant was set up at the water treatment plant of an Ontario town where the raw water has a high organic content and a history of taste and odour problems, high algal counts and elevated trihalomethane levels during the summer months.

## PHASE 1 - EXPERIMENTAL PROGRAM

Based on the literature review an experimental design was set up to evaluate the following factors which had been shown to be significant in the production of trihalomethanes during chlorination.

<u>Factor</u>	<u>Levels</u>
o DOC	o 3 water supplies - DOC=3, 6, 12 mg/L
o ozone/DOC ratio	o 4 levels - 0, 0.2, 0.75, 2.5
o delay time between ozone and subsequent chlorine residual application	o 2 levels - 3 hours, 24 hours
o type of residual applied	o 2 levels - hypochlorite and chloramine
o seasonal effects of water quality (except temperature)	o 3 seasons - summer, winter, spring runoff
o storage time after chlorine residual application	o 1 level - 24 hours

Ozonation of the unfiltered, raw water samples collected from each water supply was performed in the batch system shown in Figure 1. The applied ozone dosage was varied to establish the required ozone/DOC ratio by varying the contact time in the contact column. Absorbed ozone dosage was measured for each run to establish the actual ozone/DOC ratio. Following ozonation the water was pressure filtered through glass fibre filters and subjected to chlorination or chloramination to a half hour residual of 0.5 mg/L. These samples were stored for 24 hours before being sub-sampled for analysis.

Water samples were subjected to analysis as follows:

- o DOC
- o pH, alkalinity
- o trihalomethanes (4)
- o non-purgeable organic halogens (NPOX)
- o colour

\*Analyses for the four trihalomethanes, chloroform, dichlorobromomethane, dibromochloromethane, and bromoform were performed on an HP5840A gas chromatograph with Ni63 detector using the liquid-liquid extraction (LLE) technique. NPOX was measured on a Dohrmann microcoulometer using granular activated carbon (GAC) as the adsorbent.

Identification of the by-products of ozonation was performed by a research team at North Texas State University led by Dr. W.H. Glaze. Samples of filtered raw water and water ozonated at ozone DOC ratios of 0.2 and 2.5, were prepared from Brantford and Lindsay water during the February, 1980 sampling program. Brantford and Lindsay were selected because of the higher DOC (6-12 mg/L) contained in the raw waters as compared to that in Toronto (3 mg/L). It was not considered feasible to isolate sufficient organic material from the raw and ozonated Toronto waters for analysis.

Samples were analyzed for both volatile and non-volatile components. Volatile constituents were monitored using combined gas chromatography - mass spectrometry with computer assisted data accumulation and interpretation. A mixed bed consisting of approximately equal amounts of XAD-4 and XAD-8 was used to concentrate the volatile components. After diethyl ether elution and reduction to 500 ul, the fractions were

analyzed by SE-30 glass capillary GC/MS, i.e. gas chromatography with mass spectrometric detection.

Non-volatile constituents were examined by three modes of high performance liquid chromatography (HPLC) - size exclusion, reverse phase, and weak anion exchange chromatography. Ultraviolet absorbance and fluorescence detectors were used in most of the work, but reverse phase chromatography with an amperometric detector was also attempted.

A total of 22 samples were subjected to Ames' Salmonella bioassays for mutagenic activity in Phase 1. Water samples which had been subjected to ozonation alone, ozonation plus chlorination, and ozonation plus chloramination were tested. In all cases the organics in the samples were concentrated by rotary evaporation by a factor of 100. This process concentrated only the non-volatile fraction of the organics.

## **PHASE 1 - RESULTS AND DISCUSSION**

Statistical analysis of the detailed experimental data from the ozonation batch studies yielded the following results.

- o delay time between ozonation and subsequent chlorine residual application had no significant effect on THM or NPOX production
- o chloramine produced substantially less THM and NPOX than did chlorine whether or not pre-ozone was applied
- o THM and NPOX production appeared to be proportional to raw water DOC
- o ozone/DOC ratio had no effect on THM or NPOX production in subsequent chlorination
- o the use of ozonation significantly reduced the levels of THM and NPOX formed in subsequent chlorination as compared to chlorination alone
- o production of THM and NPOX from DOC varies from one water supply to another.

The finding that delay time had no significant effect was not expected, based on previous work presented in the literature. As there was no obvious explanation for the result, this result was investigated in depth in Phase 2.

Table 1 summarizes the detailed THM results for Phase 1 pooled according to water supply, season and ozone/DOC ratio. These data illustrate that ozone/DOC ratio has little effect on the THM levels produced in subsequent chlorination. There is a trend to reduced THM levels with increasing ozone/DOC ratio, but the trend is not significant statistically at the 95% confidence level.

Production of THM per unit of DOC is presented in Table 2. Although Brantford and Lindsay had quite different DOC's, measured THM levels were approximately equal, with both being higher than Toronto. This illustrated firstly that a general trend toward higher THM is produced from higher DOC's, and secondly that THM production per unit of DOC can vary substantially from one water supply to the next. Consequently, evaluation of ozone as an alternative disinfectant for THM reduction must be conducted on a site specific basis to account for this difference. In general however, production of THM was reduced in all three water supplies by 25% to 40% through the use of ozonation prior to chlorination to produce a residual.

Table 3 summarizes NPOX production by type of residual, water supply, and use of ozone prior to residual addition, while Table 4 presents the data in terms of NPOX production per unit of DOC. These tables illustrate that for the Brantford and Lindsay water the use of ozone substantially reduces the amount of NPOX produced in chlorination and chloramination and that the production of NPOX from DOC varies from one water supply to the next as was seen for THM production. The Toronto data appear erratic, and do not follow the trends and levels established by the Brantford and Lindsay data. The reason for this is not known.

The results of the organic identification work by GC/MS and HPLC showed that ozonation produced a wide variety of new compounds. Most of these may be rationalized in terms of oxidative cleavage of the natural humic materials in the raw waters. Higher concentrations of these materials resulted from higher ozone dosages, as expected, and also from higher DOC concentration in the raw water. Lindsay water, which had the highest DOC, also yielded the largest number of ozonation byproducts. Many of the byproducts were ketones, aldehydes or organic acids presumably formed from the cleavage of carbon-carbon double bonds by the classical Criegee mechanism. Several aromatic carboxylic acids were found, as well as many substituted phenols. These presumably were formed by cleavage of the natural aquatic humic materials.

In general, the compounds identified were in the low parts-per-billion concentration range or less, and their combined concentrations represent a small fraction of the largely uncharacterized matrix of organic carbon compounds found in natural waters. Most of the organic ozonation products found are similar to products obtained by natural oxidation processes and are probably innocuous.

The results of Ames' salmonella testing for bacterial mutagenicity showed essentially no mutagenic activity from the organics isolated by the rotary evaporation procedure. The rotary evaporation procedure recovers the non-volatile organic materials from water which have boiling points greater than 100°C. This represents in excess of 90% of the organic matter present in water supplies. The results in this study have been interpreted to indicate that this large fraction of the organics in raw and treated waters are not mutagenic under the test conditions applied in this study.

## PHASE 2 - EXPERIMENTAL PROGRAM

The bench-scale testing conducted in Phase 1 confirmed the feasibility of applying ozone for reducing the levels of THM and NPOX formed during the disinfection process. In Phase 2, a demonstration pilot plant was established at Lindsay to provide operating data representative of the normal variations in water quality and temperature which would be experienced at a water treatment plant. Of the three plants evaluated in Phase 1, Lindsay was selected because of its high DOC, wider range of ozonation by-products, and MOE plans to conduct pilot testing at Lindsay for taste and odour control.

The factors to be examined in the pilot testing were the same as in Phase 1, with the addition of temperature as shown below.

<u>Factor</u>	<u>Levels</u>
o DOC	o normal variation
o ozone dosage	o 4 levels - 0, 2.0, 7.5, 20 mg/L
o delay time between ozonation and subsequent chlorine residual application	o 3 levels - 3, 6, 24 hours
o storage time after chlorine residual application	o 3 levels - 4, 24, 72 hours
o type of residual applied	o 2 levels - hypochlorite or chloramine
o seasonal effects of water quality including temperature	o 3 seasons - winter, summer, fall



These factors were set up in incomplete factorial experimental designs for each season to facilitate statistical analysis. Table 5 presents the basic experimental design for each set of seasonal experiments.

Ozonation of the unfiltered raw water was performed in the continuous flow pilot plant system illustrated in Figure 2. The column was operated in the downflow mode so that gas flow and liquid flow were countercurrent to maximize gas transfer. Column height and residence time were typical of conventional water disinfection systems with 4.2 m (14 ft) operating water depth and 6 minutes contact time. Ozone dosage was controlled by varying the generation rate in the ozone generator. Production rate and column loss rate of ozone were monitored for each run. A small side-stream of ozonated water was withdrawn through a glass fibre filter for use in batch chlorination and chloramination tests after the appropriate delay time. These samples were then stored at the ambient water temperature for the required storage time prior to sub-sampling for analysis of a wide range of analytical parameters.

A considerable amount of analytical data was generated during the experimental program. Figure 3 illustrates the analytical data collected at each step in the pilot plant process.

## **PHASE 2 - RESULTS AND DISCUSSION**

Statistical analysis of the detailed experimental data from the Phase 2 ozonation studies yielded the following results at the 95% confidence level.

- o delay time between ozonation and subsequent chlorine residual application again had no significant effect on THM or NPOX production
- o storage time after chlorine residual application had no significant effect on THM production
- o the application of ozone as the primary disinfectant significantly reduced THM production although dosage had no significant effect in the range of 2-20 mg/L of ozone applied
- o chloramine produced significantly less THM and NPOX than did chlorine both with and without pre-ozonation
- o temperature significantly effects the production of THM and NPOX

Table 6 presents pooled data to illustrate the effect of season (temperature) and the effect of ozone dosage on chloroform and total trihalomethane (TTHM) production. Data for pre-chlorination/post-chlorination is provided for comparison. Figure 4 presents the data graphically to illustrate that ozonation application does reduce the chloroform production, but that applied ozone dosage in the range 2-20 mg/L had little effect on THM levels.

The percentage decreases in chloroform and TTHM production achieved through ozonation are presented in Table 7. When pre-ozonation/post chlorination is compared to pre-chlorination/post chlorination, reductions in chloroform and TTHM productions of 45% to 65% were achieved. As compared to post-chlorination only (no pre-ozonation or pre-chlorination), reductions of 35% to 50% were achieved. The data also indicate that simple elimination of pre-chlorination resulted in a 20% to 40% decrease in chloroform and TTHM. This has shown to be a viable alternative for TTHM reduction for raw water supplies with low algal and coliform counts. However, for water supplies with elevated micro-organism levels, pre-disinfection of some form is essential to the provision of safe drinking water.

Figure 5 presents the TTHM data normalized by DOC to illustrate the seasonal effect of temperature on the production of THM during post-chlorination.

Table 8 presents the NPOX data for the Phase 2 experiments on post-chlorination, grouped by ozone dosage and season. The data show a marked reduction in NPOX production at low ozone dosages with increasing NPOX concentrations at higher ozone dosages. This would be expected if it was assumed that destruction of existing organic chlorination sites resulted from low dosages of ozone, followed by generation of new sites as a result of cleavage of the organic matrix by excess ozone. This premise appears to be true, as mean free chlorine demand as a function of mean absorbed ozone dosage showed a pattern similar to that of the NPOX data. When NPOX was plotted against chlorine demand, a straight line relationship was found (Figure 6).

Tables 9 and 10 serve to illustrate the low levels of THM and NPOX formed when chloramine is used as the secondary disinfectant to provide a residual in the distribution system.

The most surprising findings of the study were that the delay time between pre-ozonation and post-chlorination, and storage time after chlorination had no effect on THM production. This appeared to contradict most of the published literature on THM production to date. However, it was found that the free chlorine residual had been exhausted very rapidly so that after even the shortest storage period of 4 hours, no free chlorine residual remained, and only a combined (or chloramine) residual remained.

All samples were chlorinated to a free residual of 0.5 mg/L after a half-hour as a standardized treatment of all samples. The implication of this is important for full-scale water treatment using ozone. Other researchers have found that increasing delay time and storage time have resulted in increased THM production when pre-ozonation is combined with post-chlorination at high levels of free chlorine residual. Limitation of the free chlorine residual, either by deliberate quenching to chloramine or by exhaustion as occurred in these tests, can be used successfully to control THM production.

## CONCLUSIONS

Where raw water quality is such that pre-disinfection cannot be eliminated, use of alternate disinfectants is generally recognized as one method for minimizing or eliminating THM and TOX formation. This study examined the use of ozone as an alternate primary disinfectant in combination with both chlorine and chloramine as secondary disinfectants. The following conclusions have been drawn from the study.

- 1) Ozonation has been shown to provide a substantial reduction in THM and NPOX production when combined with controlled post-chlorination. However the reduction was largely independent of applied ozone dosage in the range 2-20 mg/L.
- 2) The decision to use ozone, therefore, should be based on a need to reduce THM concentrations for public health reasons, but the selection of the applied dosage should be based on other factors such as destruction of micro-organisms, taste and odour control, and economic considerations.
- 3) As chloramine produced substantially lower THM and NPOX concentrations when applied as the secondary disinfectant, it would be the disinfectant of choice to provide a distribution system residual.
- 4) The differences in THM and NPOX production in different water supplies make pilot scale testing an important part of the selection of design criteria for the application of ozone to drinking water.

TABLES

TABLE 1: COMPARISON OF MEAN THM PRODUCTIONS - DATA  
GROUPED BY OZONE DOSAGES

		<u>O<sub>3</sub>/DOC RATIO</u>			
	DOC (mg/L)	0	0.2	0.75	2.5
<u>Brantford</u>					
Summer	6.3	48.7	23.3	29.0	18.7
Winter	5.1	221.0	73.4	121.5	30.5
Spring	6.8	121.4	129.2	114.6	51.1
Mean*	6.1	171	101	118	41
<u>Lindsay</u>					
Summer	11.4	97.7	36.4	63.4	55.8
Winter	10.8	165.5	146.0	121.0	109.2
Spring	9.4	145.0	146.2	88.5	78.9
Mean*	10.5	155	146	105	94
<u>Toronto</u>					
Summer	2.4	46.2	8.5	8.7	10.1
Winter	2.7	13.7	14.1	19.6	12.5
Spring	2.8	64.3	23.7	48.7	20.5
Mean*	2.7	39	19	34	33

\* Overall means for THM calculated from winter and spring data only

TABLE 2: THM PRODUCTION FROM DOC

		DOC (mg/L)	THM Production from DOC (ug/mg)	
			Chlorinated	Ozonated/Chlorinated
a)	Hypochlorite			
	Brantford	6.1	28.5	18.3
	Lindsay	10.5	15.4	11.4
	Toronto	2.7	14.1	8.4
b)	Chloramine			
	Brantford	6.1	0.0	0.0
	Lindsay	10.5	0.0	0.0
	Toronto	2.7	0.0	0.0

TABLE 3: SUMMARY OF NPOX PRODUCTION

	DOC (mg/L)	NPOX Production (ug/L)	
		Chlorinated	Ozonated/Chlorinated
a) Hypochlorite			
Brantford	6.1	330	128
Lindsay	10.5	262	198
Toronto	2.7	232	31
b) Chloramine		Chloraminated	Ozonated/Chloraminated
Brantford	6.1	65	45
Lindsay	10.5	114	68
Toronto	2.7	3.4	31

TABLE 4: NPOX PRODUCTION FROM DOC

	DOC (mg/L)	NPOX Production from DOC (ug/mg)	
		Chlorinated	Ozonated/Chlorinated
a) Hypochlorite			
Brantford	6.1	54.2	21.0
Lindsay	10.5	24.9	18.8
Toronto	2.7	117	15.6
b) Chloramine		Chloraminated	Ozonated/Chloraminated
Brantford	6.1	10.7	7.4
Lindsay	10.5	10.8	6.5
Toronto	2.7	1.71	15.6

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TABLE 5:            INCOMPLETE FACTORIAL EXPERIMENTAL DESIGN  
                         FOR PHASE 2

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Test	Ozone Dosage ( $x_1$ ) (mg/L)	Delay Time ( $x_2$ ) (hrs)	Storage Time ( $x_3$ ) (hrs)
1	20	24	24
2	20	3	24
3	2	24	24
4	2	3	24
5	20	6	72
6	20	6	4
7	2	6	72
8	2	6	4
9	7.5	24	72
10	7.5	24	4
11	7.5	3	72
12	7.5	3	4
13	7.5	6	24
14	7.5	6	24
15	7.5	6	24

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TABLE 6: MEAN CHLOROFORM AND TTHM PRODUCTION BY HYPOCHLORITE-  
DATA GROUPED BY OZONE DOSAGE AND SEASON

Nominal Applied Ozone Dosage	Mean Chloroform Production (ug/L)			Mean TTHM Production (umol/L)		
	March (5°C)	July (26°C)	Sept. (13°C)	March	July	Sept.
0	87.6±31.3(2)	253±38.8(6)	186.4±16.8(6)	0.784±.293(2)	2.257±.320(6)	1.592±.146(6)
2	54.1±31.3(2)	173±38.8(4)	132.0±18.5(4)	.507±.193(4)	1.623±.338(4)	1.146±.156(4)
7.5	53.2±13.2(7)	175±27.9(7)	125.6±14.6(6)	.500±.127(7)	1.601±.234(7)	1.090±.126(6)
20	39.2±7.4(4)	154±16.4(4)	105.3±29.8(4)	.354±.073(4)	1.438±.145(4)	.907±.256(4)
0(Pre NaOCl)	-	320±33.6(9)	319.6±40.1(8)	-	2.838±.278(9)	2.720±.346(8)

Note: Data presented as Mean ± Standard Deviation (No. of data points in mean)

TABLE 7:        DECREASES IN CHLOROFORM AND TTHM PRODUCTION  
                      RESULTING FROM MODIFYING OZONATION  
                      AND CHLORINATION CONDITIONS

Nominal Applied Ozone Dosage (mg/L)	Decrease in Chloroform Production (%)			Decrease in TTHM Production (%)		
	March	July	Sept.	March	July	Sept.
a) Relative to Pre- plus Post-Chlorination						
0	-	21	42	-	20	41
2	-	46	59	-	43	58
7.5	-	45	61	-	44	60
20	-	52	67	-	49	67
b) Relative to Post-Chlorination						
2	38	32	29	35	28	28
7.5	39	31	33	36	29	32
20	48	39	44	55	36	43

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TABLE 8:            NPOX CONCENTRATIONS: DATA GROUPED  
                         BY OZONE DOSAGE AND SEASON

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Nominal Applied Ozone Dosage (mg/L)	Mean NPOX Production (ug/L)		
	March <sup>1</sup>	July <sup>2</sup>	September <sup>2</sup>
0	152±80(2)	153	52
2.0	60±55(4)	88	20
7.5	100±33(7)	65	45
20	137±60(4)	112	35

<sup>1</sup> Data presented as Mean ± Standard Deviation (Number of data points in mean)

<sup>2</sup> Data are for analysis of random sample at each ozone dosage

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TABLE 9: MEAN CHLOROFORM CONCENTRATIONS  
OBSERVED DURING CHLORAMINATION

Nominal Applied Ozone Dosage (mg/L)	Water Source	Mean Chloroform Concentration (ug/L)		
		March	July	September
0	Raw	12*	6.04±3.50 (6)	2.49±.46 (6)
	Treated	0*	4.93±1.54 (5)	3.40±1.78 (6)
2.0	Raw	.08±.15 (4)	6.19±4.11 (4)	2.77±.53 (4)
	Treated	.02±.02	3.56±2.11 (4)	5.54±3.30 (2)
7.5	Raw	ND (7)	5.96±3.49 (7)	2.18±.38 (7)
	Treated	.08±.09 (7)	5.74±3.37 (7)	3.24±.76 (7)
20	Raw	.06±0.11 (4)	4.76±2.25 (4)	2.50±.61 (4)
	Treated	.06±0.05 (4)	5.62±2.44 (4)	2.66±.58 (3)

\* Insufficient data for statistical interpretation

TABLE 10: NPOX PRODUCTION BY CHLORAMINATION

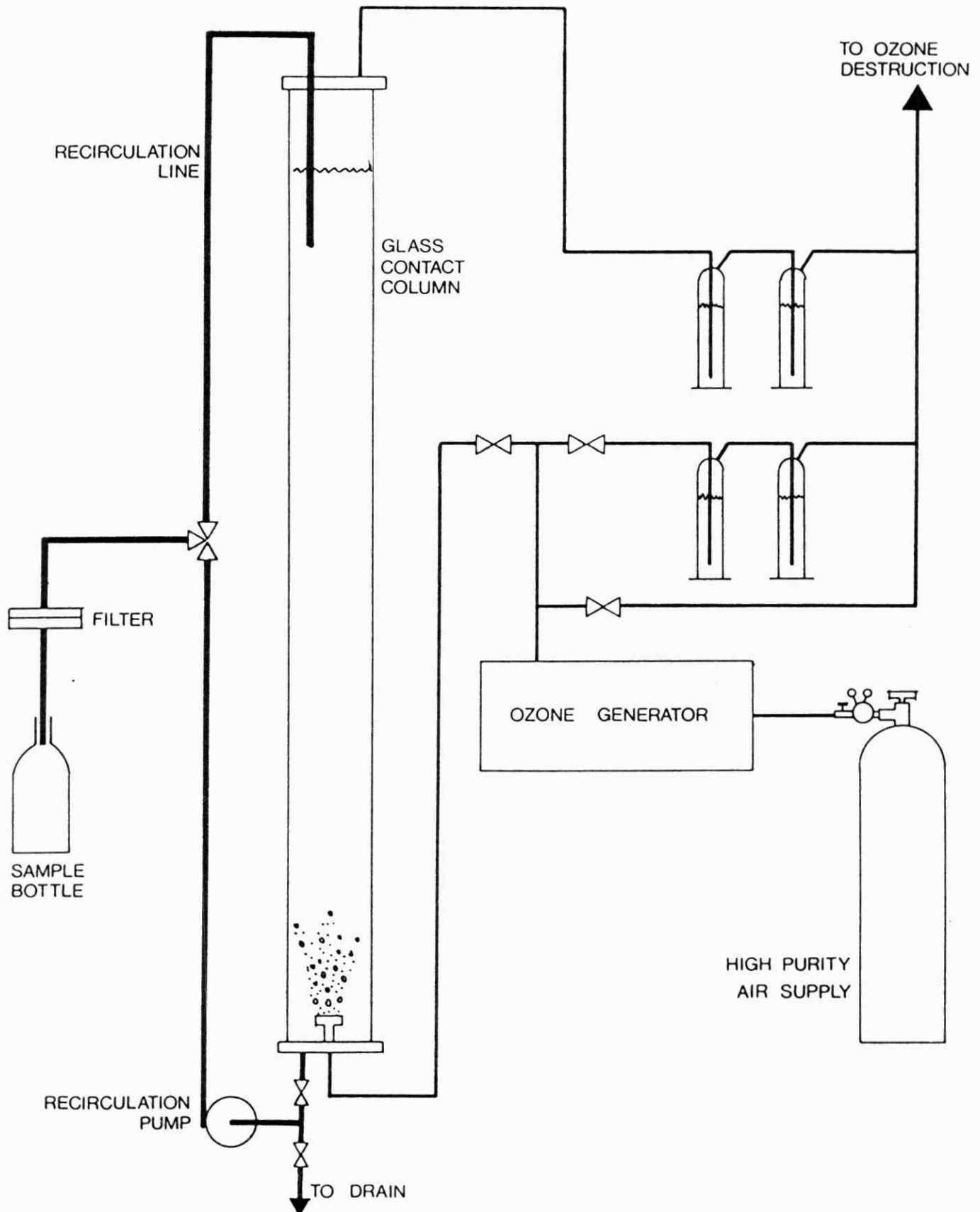
Nominal Applied Ozone Dosage (ug/L)	NPOX Production (ug/L)		
	March <sup>1</sup>	July <sup>2</sup>	September <sup>2</sup>
0	5.2±7.4 (2)	0.9	ND
2.0	ND	0.7	2.5
7.5	1.1±2.9 (7)	5.8	ND
20	ND	ND	ND

<sup>1</sup> Data presented as Mean ± Standard Deviation (Number of data in mean)

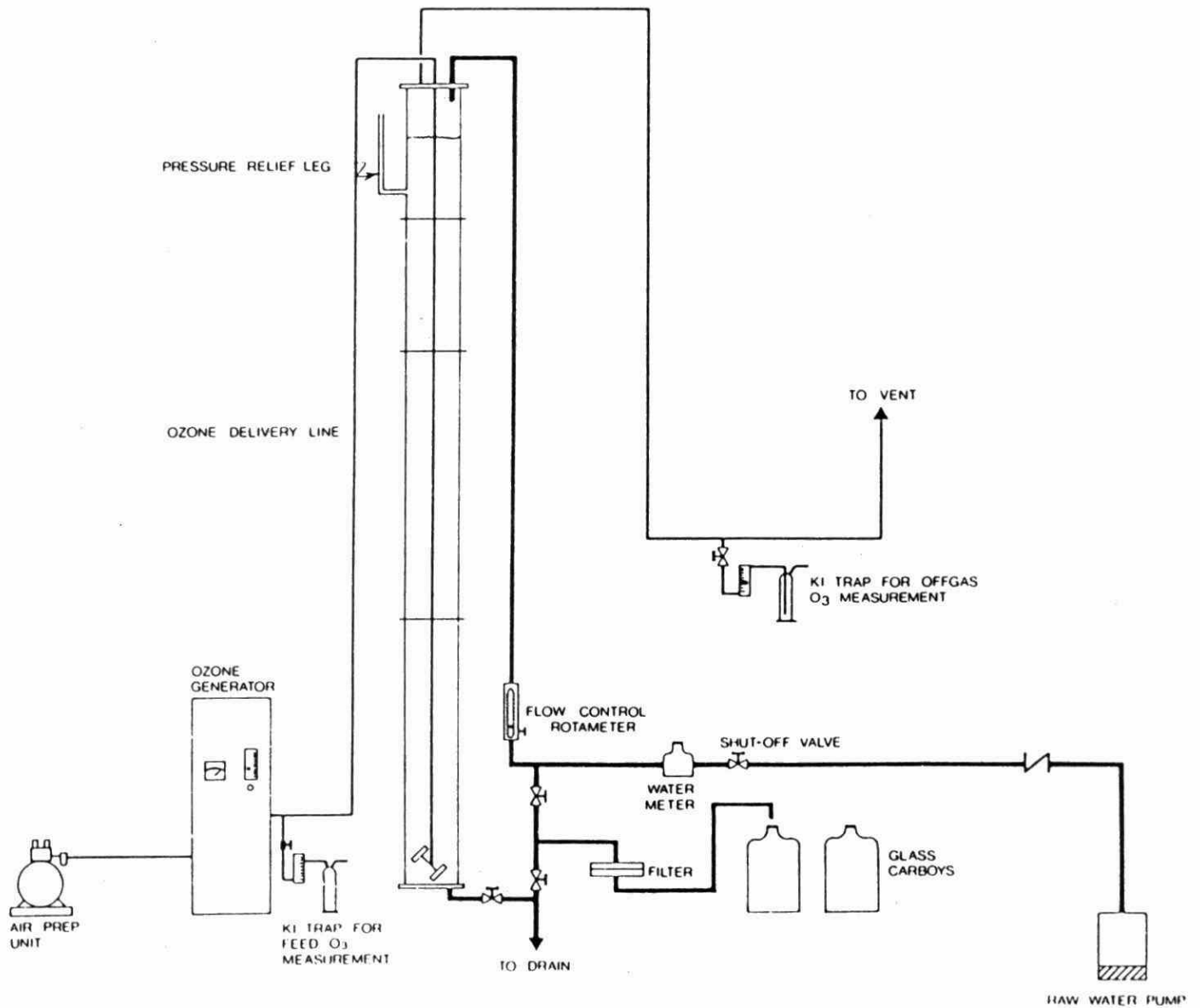
<sup>2</sup> Data are for analysis of one random sample at each ozone dosage

**FIGURES**

**SCHEMATIC OF BATCH OZONATION SYSTEM**

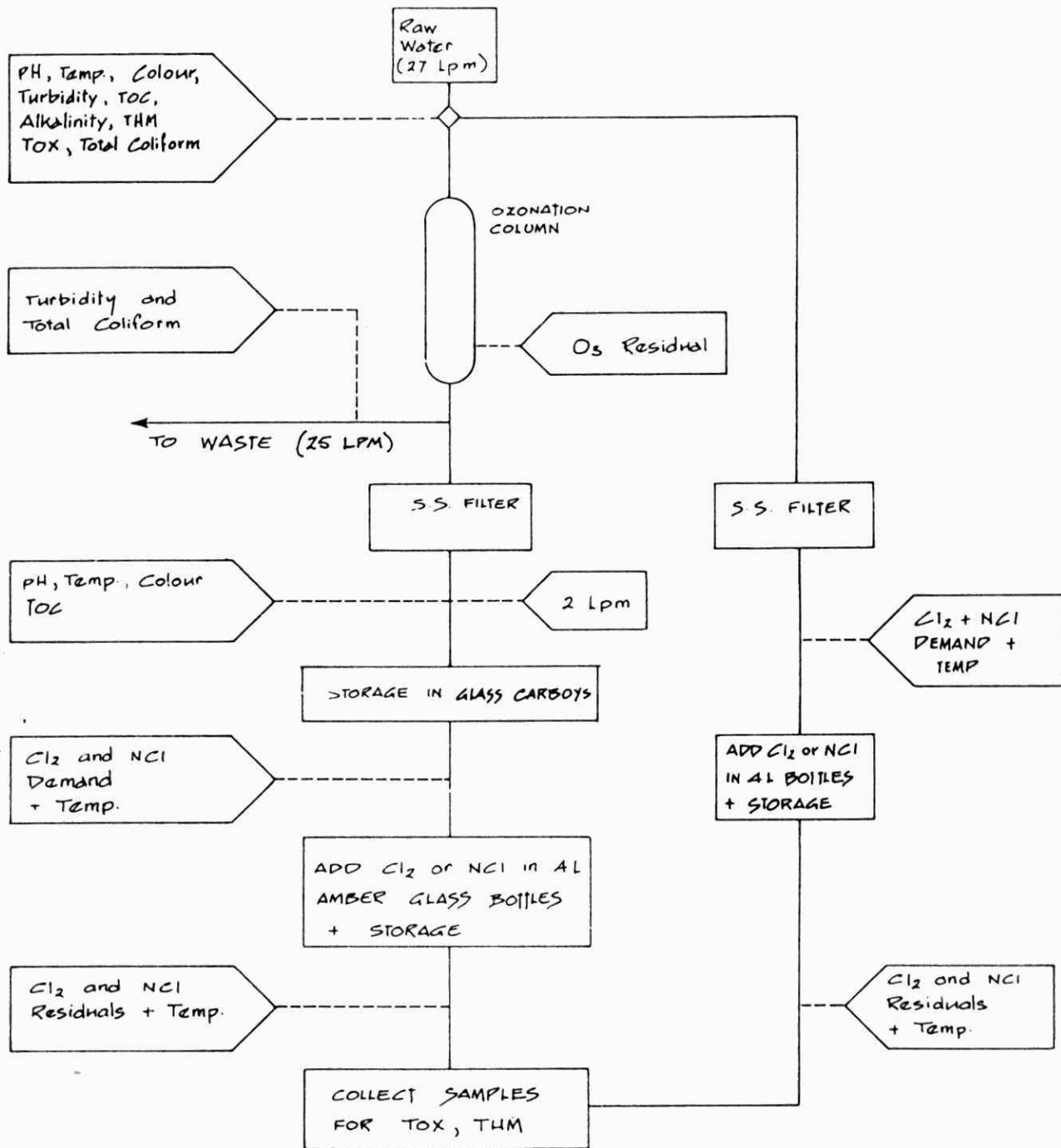


# SCHEMATIC OF OZONE PILOT PLANT SYSTEM

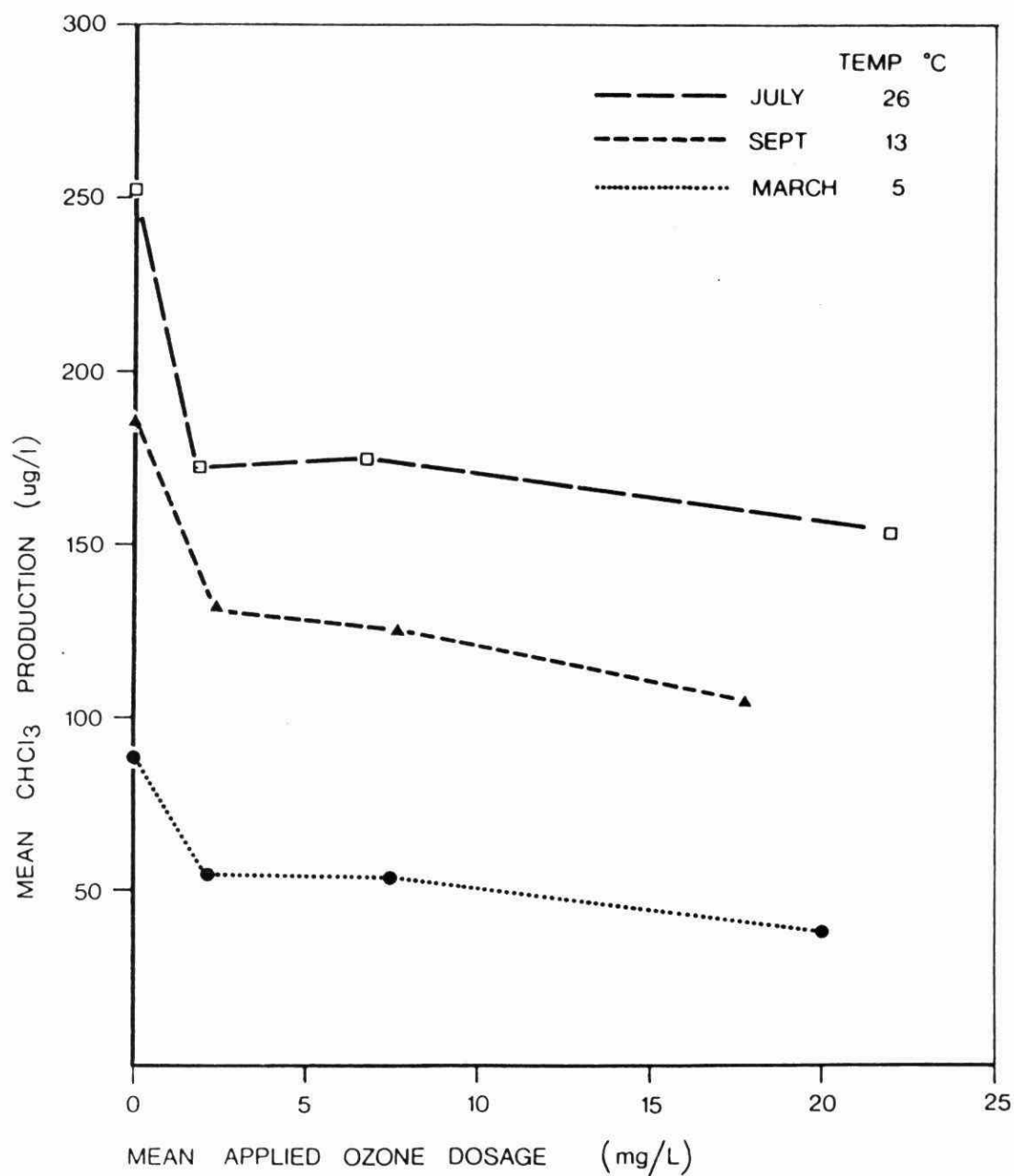




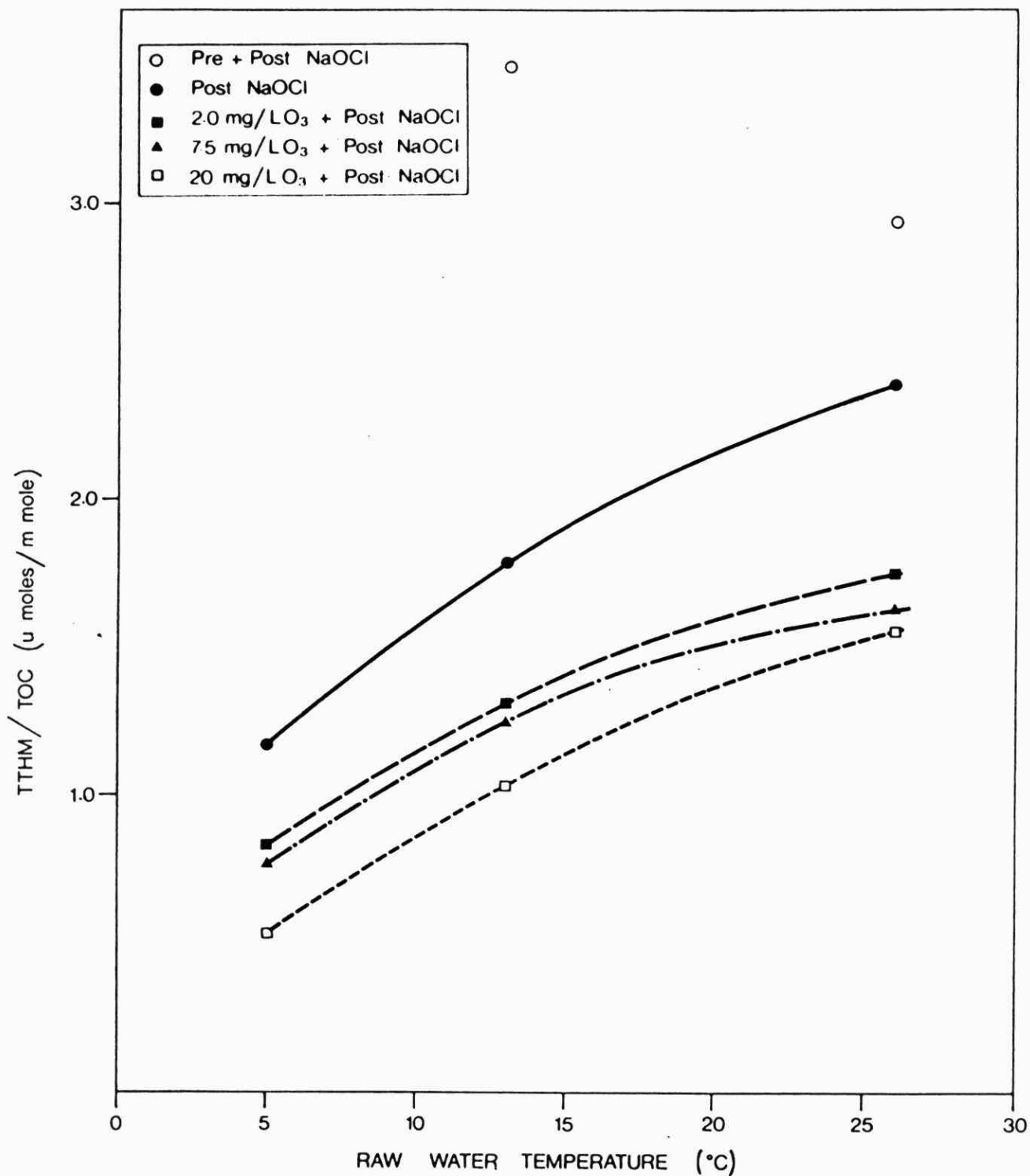
# OZONE PILOT PLANT BLOCK DIAGRAM



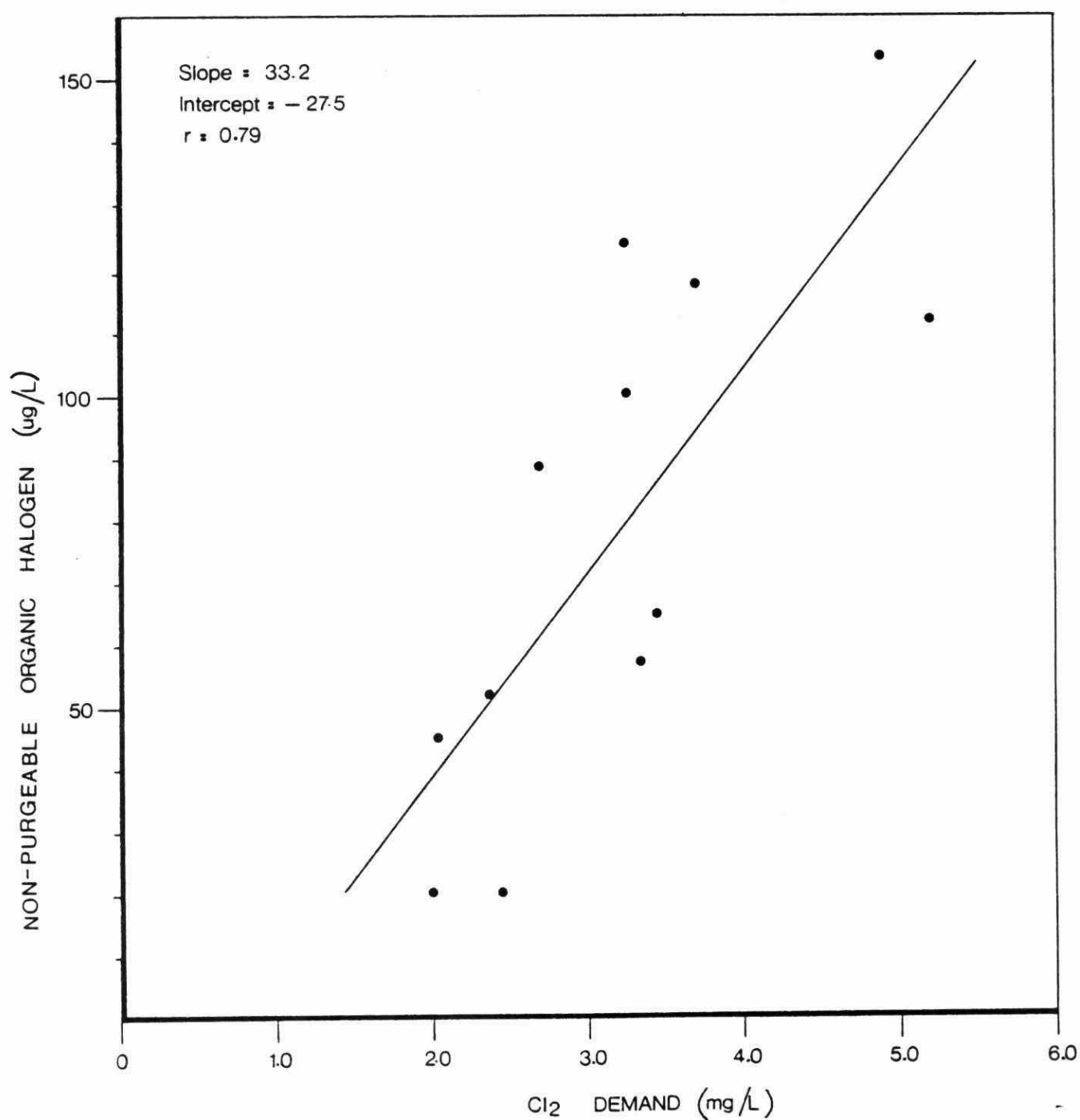
# EFFECT OF PRE-OZONATION ON CHLOROFORM PRODUCTION IN POST-CHLORINATION



## EFFECT OF TEMPERATURE ON TTHM PRODUCTION FROM TOC



# EFFECT OF CHLORINE DEMAND ON NON-PURGEABLE ORGANIC HALOGEN PRODUCTION



EVALUATION SEQUESTRATION OPTIONS FOR  
IRON AND MANGANESE CONTROL

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Ministry of the Environment

Evaluating Sequestration Options for Iron and Manganese Control

Filtration removal is not the only procedure effective for treating excess iron and manganese in potable water supplies. In fact, filtration itself is not always effective. A Nebraska State study by Anderson & Ali<sup>1</sup> as recent as 1970 showed that of some 29 filtration plants surveyed (75% of the state's total), 18 (almost 2/3rds) were not meeting the desired water quality criteria for iron and manganese (0.3 mg/L Fe and 0.05 mg/L Mn respectively).

Similar ailing filter plant performances in Ontario resulted in further study of this problem where it was confirmed that elevated silica in the raw water sometimes interfered with filtration removals. In fact, the data led directly to the use of sodium silicate addition as a practical sequestrant for stabilizing iron or manganese in a supply rather than applying filtration<sup>2</sup>. By 1980, for example, Ontario have more than 120 municipal water systems employing a silicate sequestration technique. The lower cost of sequestration was popular; but sometimes the impracticability of filtration for the supply was a factor.

Anomalous iron-bearing supplies unsuitable for filtration treatment continue to be encountered in the Province. Two wells at Ignace, for example, originally resisted any filtration removal of a 2.8 mg/L iron content although air or chlorine contact would tint the water brown. The brown tint however could be avoided if silicate sequestrant were added at about 5 mg/L SiO<sub>2</sub>.

The Victoria Street well at Cookstown was similar with a 1 mg/L iron content developing a clear amber tint on oxidation; but where filtration, ion exchange softening, or room-temperature retention for over a month would not drop any of the iron out of the water. Also, recent

samples sent to the Ministry from Gananoque and Portland Twp. showed atypical iron content. Again, filtration, ion exchange softening, or month-long standing would not remove most of the colour-producing iron. The consultant involved, however, found that anion exchange resins had a considerable, though somewhat variable, success for removing the iron involved.

Clearly, water-borne iron (and manganese) in natural waters appears to be surprisingly complex and not fully understood. Such uncertainties should also be borne in mind when considering the following sequestration alternatives.

Up to four different sequestration procedures appear practical to date. These procedures are anything but equivalent so that for differing water quality and treatment circumstances, a treatment of preferred merit can often be discerned. These sequestration procedures might be summarized as follows:

[A] Sodium Hexametaphosphate (and/or polyphosphate)

-Hexametaphosphate or polyphosphate of AWWA Specifications

#B502 and B503-78 added before chlorination or air contact

-Optimum application: at least 3 to 5 minutes before chlorine  
or air contact

-Dosage: 2 to 5 times iron content

-Limits: 1 to 2.0 mg/L iron content as Fe

Origin: early use purported 1936-1937, Delaware, Ohio

[B] Sodium Silicate Procedure 1

-Addition of Liquid Sodium Silicate ( $\text{SiO}_2/\text{Na}_2\text{O} \approx 3.22$ )

Solution meeting AWWA specification #B404-80 prior air  
contact, but during chlorination

-Optimum application: at chlorination (rapid oxidation)  $\pm$  15 seconds

-Dosage: 1 to 20 mg/L silicate (as  $\text{SiO}_2$ )

-Limits: 2.5 to 3.0 mg/L iron content as Fe

-Origins: MOE tests at Markham in 1969

[C] Sodium Silicate Procedure 2

-Addition of Liquid Sodium Silicate ( $\text{SiO}_2/\text{Na}_2\text{O} \approx 3.22$ )

Solution meeting AWWA Specification #B404-80

prior air or chlorine contact

-Optimum application: with chlorination of water to suppress  
biological fouling

-Dosage: mg/L  $\text{SiO}_2$  addition =

$$[(\text{total CaCO}_3 \text{ hardness}) \times 0.6 + 1.07 \\ (\text{mg/L Fe} + \text{Mn})]$$

-[mg/L of soluble raw water  $\text{SiO}_2$ ]

-Limits: Hardness <30-40 mg/L  $\text{CaCO}_3$

Iron up to 10 mg/L Fe

-Origins: MOE development tests at South River, 1978-1982

[D] Hydrogen Peroxide (Manganese Problems only)

-Hydrogen peroxide at or prior to chlorination

-Optimum application: with chloramine chlorination

-Dosage: Maximum mg/L  $\text{H}_2\text{O}_2$  for addition =  
(mg/L Mn)  $\times$  0.61

-Limits: Normally no more than 0.3 mg/L Mn

Origins: MOE tests at Woodbridge and Wellington in 1977.

SEQUESTERANT CHEMISTRY

Phosphate sequestrants appear to combine with iron and manganese prior to the oxidation of these ions to the precipitable states by chlorine or air. Much of their effectiveness seems to result from inhibiting the oxidation of these metal ions in their sequestered state. Lowered chlorine demand of the treated water and an improved effectiveness when the sequestrant is added some 3 to 5 minutes before air or chlorine

contact appear to be consequent observations of such chemistry.

In contrast, silicate sequestrant is optimally added at the point of chlorination prior to any contact of the water by air. Silicate, it seems, combines best with iron and manganese after their oxidation such as by chlorine. The silicate, however, must be added quickly before the freshly oxidized ions obtain opportunity to polymerize into high molecular weight materials to form precipitates. Prompt addition after chlorination appears to allow silicate's combination with monomer metal hydroxides to quench the secondary reactions leading to floc particle formation.

Silicate also appears to combine with available hardness ions although at a slower rate than its combination with higher valence iron and manganese contaminants. Thus, when silicate is added much in advance of water chlorination, it may lose virtually all of its activity by hardness ion combinations prior to chlorination formation of oxidized iron and manganese. Unlike the phosphate application, silicate addition efficiencies are greatly diminished by any significant delay between silicate injection and chlorination.

Silicate reactivity in a water is retained, however, in any supply where the natural plus added silica content exceeds the equivalent available hardness. Once the silica level exceeds the chemical equivalent of 6 mg/L  $\text{SiO}_2$  for every 10 mg/L  $\text{CaCO}_3$  hardness, then any additional silica content tends to remain free and reactive for combining in a one-to-one ratio, with iron or manganese ions - even before oxidation. The dosing, or even the natural occurrence of, stable free silica in a water represents the essential chemical difference of the "Silicate Procedure 2" as compared to the "Silicate Procedure 1" treatment.

With a hardness-exceeding silica content (more easily possible with soft waters) iron and manganese become sequestered, with or without



chlorination. Free silica levels can allow almost any health-permissible level of iron or manganese to be retained in stable solution for consumer use. Chlorination, however, would be mainly advised for the purposes of avoiding biological fouling which might be stimulated by possible oxidation of any yet unoxidized iron or manganese.

The chemistry of hydrogen peroxide for manganese control is still not well understood. Test-book literature tends to suggest that hydrogen peroxide would oxidize manganic ion to an unstable oxide level which in turn breaks back down to the divalent (reduced) ion. Peroxide effects such reductions with other chemicals such as silver oxide (reduced to silver) or chlorine residuals (reduced to chloride ion).

Soluble manganous salts from laboratory or raw water sources can usually be oxidized to the brown precipitating form with relative ease by chlorine or ozone. But, the "divalent manganese" formed by peroxide treatment proves highly resistant to such oxidations - being especially refractory to ozonation. In keeping with the periodic table tendency of elements numbers 22, 23 and 24 (titanium, vanadium and chromium) to form ions reactive with peroxide, it would not be illogical to find manganese (#25) with a similar property. Certainly the peroxide treatment for manganese behaves like a sequestration solubilization where there is a general reprecipitation in response to treatment chemicals strongly destructive of hydrogen peroxide (ie. free chlorine residuals or potassium permanganate).

#### OVERALL CONSIDERATIONS

Field experiences along with some inferences from each sequestrant's basic chemistry lead to certain summary advantages and disadvantages for each sequestration technique, such as:

##### Polyphosphates

- Advantages 1) useful where ions already resist oxidation
- 2) effective in absence of chlorination

- Disadvantages
- 1) 3-5 minutes pretreatment best before chlorination
  - 2) slight haze turbidity with some waters
  - 3) fouling energy in unoxidized ions remains
  - 4) fouling encouragement possible with phosphate nutrient
  - 5) up to 2 mg/L Fe + Mn only
  - 6) generally not as stable as silicate sequestration
  - 7) trial and error dose determination

#### Silicate Procedure 1

- Advantages
- 1) relatively stable sequestration (especially Mn)
  - 2) low cost "water-native" chemical
  - 3) lowers biofouling potentials during ion oxidations
  - 4) concurrent with chlorination
  - 5) up to 3 mg/L Fe + Mn
- Disadvantages
- 1) Concurrent chlorination essential
  - 2) not applicable to oxidation-inhibiting waters
  - 3) seldom applicable to manganese
  - 4) trial and error dose determination

#### Silicate Procedure 2

- Advantages
- 1) exceptionally stable sequestration (all ions)
  - 2) chlorination optional and optionally locatable
  - 3) excellent corrosion protection in oxidizing waters
  - 4) may control in excess of 10 mg/L Fe and 2 mg/L Mn
  - 5) dose requirement easily calculatable
- Disadvantages
- 1) few water supplies qualify with low enough hardness
  - 2) treatment may sequester health-affecting levels
  - 3) chlorination for antifouling may still be needed

### Hydrogen Peroxide

- Advantages
- 1) effective on all "forms" of natural manganese
  - 2) low level, "water-native" chemical treatment
  - 3) calculatable maximum dose
- Disadvantages
- 1) treats manganese only
  - 2) may require combined chlorine residuals
  - 3) practical level for consumer use about 0.3 mg/L Mn

### PARAMETERS AIDING TREATMENT SELECTION

A number of water quality tests can prove significant in facilitating an effective treatment selection from the options available. Comprehensively test parameters may include:

All nitrogens: free ammonium, total Kjeldahl, nitrite  
and nitrate  
(as contamination tracers and biofouling factors)

"Limestone saturation" tests: pH, alkalinity, calcium and  
magnesium (to assess corrosivity and oxidizability  
of any iron and manganese)

"Fouling factor" components: iron, manganese, organic carbon  
(TOC or DOC) and silica (for estimating  
precipitation and biofouling potentials)

"Tracer ion" tests: conductivity, sulphate, chloride, sodium  
and sometimes potassium (for chemical profile  
source tracing; sulphate also as biofouling  
potentiator)

Field Observations: (Raw and Treated Water) turbidity, colour,  
odour, flavour, dissolved oxygen, and chlorine  
residuals

The significance of the latter "field observations" can hardly be overemphasized. For example, if a water's excess iron were giving rise

to colour and turbidity appearance prior to any air contact, it would represent a type of iron content not controllable by sequestration. Filtration would normally be needed. Often, however, precipitated iron from a well may occur only at the commencement of pumping, so that if the initial few minutes of pumpage were discarded, the rest of the yield could effectively be sequestered.

Similarly, unpleasant flavours can sometimes be reduced by aeration-filtration while trace sulphide odour can indicate that effective silicate treatment would be possible. Dissolved oxygen and chlorine residual tests where pertinent to potential fouling conditions may also be done on-site.

#### TREATMENT SELECTION

Getting through the tangle of considerations for judging those treatment options which might work best with each water can be exemplified by one approach taken by our Water Technology Section. The following considerations appear to resolve the main selection "watersheds".

##### A) IRON TREATABILITY FACTORS

###### 1. Soluble iron levels?

- field observations of low turbidity raw water needed to assure soluble iron suitable for sequestration - otherwise Filtration needed.
- less than 2.0 mg/L Fe may allow Polyphosphate treatment
- less than 3.0 mg/L Fe may allow Silicate 1 procedure
- greater than 3.0 mg/L Fe requires either Silicate 2 or Filtration processes
- greater than 10.0 mg/L Fe, Filtration or Coagulation - Filtration may be more practical

###### 2. Natural silica content compared to total hardness?

- waters with silica content equal or greater than [(Total  $\text{CaCO}_3$  hardness) - 16] x 0.6 in mg/L  $\text{SiO}_2$  will allow

Silicate 2 sequestration - (assuming 10 mg/L Fe limit for potable use and the addition of more than 20 mg/L  $\text{SiO}_2$  likely troublesome).

Filtration treatment would also be compromised strongly by water quality of the type thus favourable to Silicate 2 sequestering.

-waters with absolute silica levels in excess of 15 mg/L  $\text{SiO}_2$  (7 mg/L Si) may demonstrate increasing difficulties towards

Filtration removal of iron with increasing silica levels. On-site Filtration tests may be advisable for high silica supplies.

### 3. Corresponding alkalinity and hardness contents?

-the essential rapidity of iron oxidation required for effective Silicate 1 sequestration treatment appears hindered by any bicarbonate ion (alkalinity) in excess of the total hardness complement.

-such hardness-free alkalinity may commence difficulties from about 5 to 10% level of the total alkalinity given a 2.5 - 3.0 mg/L Fe water.

-slowed iron oxidation effects may also hinder Filtration removal.

-trace sulphide odour detected in the raw water may fully or partially negate above relationship to re-establish efficient Silicate 1 or Filtration procedures.

-on-site treatment tests may be useful here for indeterminate assessments.

### 4. Availability of biofouling energy sources?

-sequestration-treated water is generally more susceptible to biological fouling both by retention of chlorine-shielding iron and manganese minerals and the lack of organic removal and/or stabilization opportunity.

-the juxtaposition of significant biologically oxidizable materials such as methane, organic carbon, organic nitrogen compounds, ferrous and manganous ions with biologically usable oxidants such as

dissolved oxygen, nitrates, or high sulphates may rule out sequestration treatments.

- Polyphosphate sequestration is least able to resist fouling influences.
- Aeration-filtration may remove methane and stabilize dissolved organics in absence of prechlorination. Strong superchlorination of filter backwashwater would be recommended to avoid excess filter bed fouling.

## B) MANGANESE TREATABILITY FACTORS

### 1. Chlorination response?

- To date, the response of naturally occurring manganese to oxidation has proven to be exceptionally unpredictable. About 2/3rds of such waters containing somewhat more than the desired 0.05 mg/L Mn limit, yield no significant problems upon chlorination.
- bottle tests for chlorination response requires relatively fresh water samples but need not be conducted on-site as would be the case for iron.
- manganese quickly oxidized by air or chlorination (colour development within 30 seconds by chlorine) should be sequesterable by the Silicate 1 procedure. It is also easiest to remove by Filtration. Polyphosphate sequestering only sometimes works.
- manganese only sluggishly oxidized by chlorine is best treatable by Polyphosphates or manganese greensand filtration.
- the above observations are valid for both free and combined chlorine residuals. By superchlorination or ammonium salt addition, both types of chlorination response can be explored towards allowing any preferred treatment possibility as described.

-warning: it seems relatively common to find more than one type of manganese (in terms of chlorine response) in any supply. Individual considerations for each variety of manganese can sometimes be required.

2. Natural silica content compared to total hardness?

-although limited to laboratory experience, it appears that manganese, like iron (see A. 2), becomes solubly captured by hardness-free silica both before and at oxidation. High silica, low hardness waters as described for iron may successfully use the Silicate 2 procedure. Limits of 2.0 mg/L Mn and 20 mg/L  $\text{SiO}_2$  of added silicate are advised for potable supplies. Filtration removal would be most difficult if at all possible with such water.

3. Corresponding alkalinity and hardness contents?

-as with iron, manganese oxidation appears highly inhibited in waters containing more bicarbonate (alkalinity) than total hardness equivalents - and manganese is generally much slower to oxidize to begin with. Should any sequestrant be needed, Polyphosphate would be first choice. Manganese greensand Filtration might be a second option.

-waters with hardnesses considerably greater than the corresponding alkalinities appear essential before there is possibility of manganese oxidation being rapid enough for useful Silicate 1 sequestrations. Sequestration may be practical even if partial in some circumstances. Bottle tests are advised to remove the uncertainties involved. Filtration procedures possible subject to other conditions.

4. Trace raw water sulphide?

-in three out of three cases, a trace sulphide odour (not high enough for analytical determination) in the raw water correlated

with highly successful Silicate 1 sequestration of the manganese. Such waters would also show unusually high efficiencies for iron sequestration. This easy oxidizability of the manganese in "sulphide" supplies would overrule any treatment reluctances based on alkalinity-to-hardness relationships. Such waters would also be uncomplicated in yielding precipitates suitable for filtration removal.

5. Manganese content below 0.3 mg/L Mn?

- Hydrogen Peroxide appears as an excellent "solvent" for oxidized manganese - even after precipitation. Provided combined chlorine residuals are used (to avoid rapid peroxide destruction), peroxide addition can be relied upon to sequester any precipitating concentration. Peroxide-destroying treatment chemicals, however, such as permanganate and free chlorine (but not ozone) tend to reprecipitate peroxide-treated manganese.
- consumer end-use involving strong chlorination for laundry or swimming pools tends to limit Peroxide use to those waters containing 0.3 mg/L Mn or less in practice.
- the use of non-chlorine bleaches and a lack of swimming pool use might allow higher manganese levels being carried by Peroxide ie. 0.5 mg/L Mn.
- Peroxide may control manganese not controlled by competing procedures including Filtration.
- excess Peroxide may leach manganese solids from water systems previously coated by earlier problems.

6. Availability of biofouling energy sources?

- the continued presence of manganese in biologically susceptible water as treated by sequestration may still assist fouling organisms to resist chlorination suppression. In comparison with iron,



manganese would be less active and unlikely to contribute directly to precipitation unless dissolved oxygen or nitrate levels could persist in the fouled supply.

- sequestration, however, does lower fouling potentials where manganese (and/or iron) minerals can be made less available for biological utilization.
- Silicate 1 appears to tie up available manganese best.
- Peroxide-treated manganese appears more available.
- Phosphate-treated manganese may be more available still.
- Aeration-Filtration can have advantages in stabilizing biofouling potentials even if all the manganese proves not removable.

#### Biological Fouling Assessments

In comparison with filtration treatment, sequestration procedures are normally less promising on those waters most prone to biological fouling. Once water quality degradation becomes initiated, the causative micro-organisms may find they can acquire iron and manganese minerals (as still present) towards building up defences against chlorination and increasing fouling activity all the more. In contrast, effective filtration treatment may remove iron and manganese and in process also diminish some of the troublesome organic content by those organic contaminants that become adsorbed onto removed precipitates. Filters can also be used in a preaerated, non-chlorinated mode to become biologically active for stabilizing organics not so easily removed on precipitates.

Identification of those waters likely to have significant fouling difficulties still remains an imprecise art. Critically significant organic nutrients, for example, are normally just grouped within "organic carbon" tests and in any event would comprise an uninterpretable mixture as influenced by a wide variety of trace minerals and physical circumstances.

Behind every biological degradation of water quality will be found an "energy couple", consisting of an oxidizable substrate (food) plus a suitable respiratory oxidant.

The biological fouling energy available to degrade water quality depends as much upon the "fuel energy" per unit quantity of contaminants as it depends on the concentrations of the contaminants. In order of apparent decreasing energy value, the common oxidizable substrates rank in the order of:

Organic carbon > Reduced Sulphur > Ferrous ( $\text{Fe}^{2+}$ ) ion >  
Manganous ( $\text{Mn}^{2+}$ ) ion > Ammonium ( $\text{NH}_4^+$ ) ion

Considering organic materials, in particular, directly caused difficulties from them might arise at levels as low as 5 mg/L organic carbon (TOC or DOC tests) or about 0.20 mg/L organic nitrogen (Total Kjeldahl minus free ammonia) or about 3 litres of methane gas per cubic meter of water. While exceeding these values may not guarantee fouling problems, approaching about double the amounts rarely avoids difficulties.

Organics most likely to cause difficulties often have a mechanism by which they can collect together at high concentrations for accelerated bacterial activity. Excess methane may form bubbles at sites of lower hydraulic pressure while other materials may gather in deposited pipeline sludges and on pipeline walls. Very soluble organics tending not to concentrate seem to show more overall "stability" in this sense.

In absence of biologically usable oxidants, oxidizable substrates at any level cannot cause problems. The most common oxidants, however, can also be listed in rank of decreasing energy availability; such as

Oxygen > Nitrate ( $\text{NO}_3^-$ ) ion > Manganic ( $\text{Mn}^{4+}$ ) ion > Ferric ( $\text{Fe}^{3+}$ ) ion > Sulphate ( $\text{SO}_4^{2-}$ ) ion

Notably, iron and manganese occur in both lists for "energy couples" showing energy release during oxidation and then more energy










available in the oxidized precipitate ions being able to oxidize the organic material gathered in by such precipitation.

"Energy couples" for causing fouling problems can occur with single wells yielding water from more than one aquifer. The blending of waters from different wells in the distribution system is another hazard as is the blending of anaerobic well water with aerobic surface water supplies. Table I shows examples of some of the common energy mixtures that can cause problems.

#### Summary

- 1) It would appear that sequestration procedures are a needed set of alternatives to standard filtration techniques for solving iron and manganese difficulties. Filtration, moreover, does not work on all waters and sequestration technology is becoming increasingly applicable.
- 2) Sequestration treatment design requires increased attention to on-site test observations. Field test results on both raw and treated water can often not be duplicated back at a central laboratory facility.
- 3) On-site bottle tests for sequestration are very useful for estimating water treatability. Such tests, however, do not measure biofouling potentials which must be estimated by a relatively complete set of analyses both for the supply in question and any others proposed for blending.

# TABLE 1: AQUIFER-INCOMPATIBLE COMPONENTS

		O <sub>2</sub>	NO <sub>3</sub> <sup>-</sup>	Mn <sup>++</sup>	NO <sub>2</sub> <sup>-</sup>	Fe <sup>++</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>=</sup>	S <sup>=</sup>	CH <sub>4</sub>
Oxygen	O <sub>2</sub>			X	X	X	X		X	X
Nitrate	NO <sub>3</sub> <sup>-</sup>			X		X	X		X	X
Manganese	Mn <sup>++</sup>	X	X						X	
Nitrite	NO <sub>2</sub> <sup>-</sup>	X					X		X	X
Iron	Fe <sup>++</sup>	X	X						X	
Ammonium	NH <sub>4</sub> <sup>+</sup>	X	X		X					
Sulphate	SO <sub>4</sub> <sup>=</sup>									X
Sulphide	S <sup>=</sup>	X	X	X	X	X				
Methane	CH <sub>4</sub>	X	X		X			X		

An "X" matching of raw water components in this table indicates additional aquifer contributions (assuming suitable analytical procedures). Except for iron and manganese with sulphide combinations, biological "Energy Couples" are indicated.

## References

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SURFACE PHOTOCHEMISTRY OF ADSORBED ORGANIC SPECIES

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ABSTRACT

The chemical, and hence toxicological, consequences of light falling on organic species of environmental interest (pesticides, PAH) adsorbed on particulate matter depend on the physical processes available to these species. We have demonstrated, for the first time, that PAH and organic free radicals adsorbed on dry silica gel can undergo translational motion, and so take part in bimolecular reactions.

## INTRODUCTION

As both analytical techniques and knowledge of the environment improve, trace pollutants are becoming a cause of increased concern and study. Of particular note are those compounds that accumulate in biota, thus increasing effective concentration and exposure. Amongst this group are a number of known carcinogens which fall into the categories of polycyclic aromatic hydrocarbons (PAH) or pesticides.

Also able, in principle, to increase effective concentrations of the pollutants is the adsorption of these species from the atmosphere and from water onto the surface of solid particulate matter, i.e. silica, alumina, aluminosilicates and carbon. Such particles are then exposed to the action of ultraviolet light whereby they may be chemically transformed. The photochemical processes available to these substances are, in essentials, unknown, and as a consequence the change in toxicity cannot be predicted. Only as regards oxidation of PAH has a bare beginning been made (inter alia, 1-6)<sup>\*</sup>, the photochemical study of adsorbed pesticides lagging behind (inter alia, 7,8). In fact, the photo-oxidation of such a simple compound as anthracene is greatly accelerated when adsorbed on particulate matter over the process occurring in solution. The reaction is of considerable complexity

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<sup>\*</sup> Numbers in brackets designate References at the end of the paper.



and the chemical modifications induced by adsorption forces are not understood. It is clear that these principles must be uncovered if the fate of adsorbed PAH and pesticides under the action of light is to be determined. With such guidance the possible consequences of new pollutants can reasonably be predicted.

Reflection reveals that adsorption on a surface may modify photochemical behaviour in two senses. Firstly, the binding forces (dispersion, electrostatic, hydrogen bonding) may modify the electronic polarisation and polarisability so that the molecule's inherent reactivity is modified. Such must be the case in photoinduced oxygenation. Either unimolecular processes change, or the mode of reaction with an ubiquitous reagent (oxygen, water) is altered.

Secondly, bimolecular processes may occur. For this to take place translational movement of the adsorbed molecule is required (concentrations are too low to permit a statistically significant number of contiguous molecules) during the lifetime of the excited state. When the present researches were undertaken no information was available concerning this possibility for closed shell molecules, and little concerning the behaviour of free radicals (9-11). Here, from the linewidth and shape of the E.P.R. signal it has been concluded that there is rotational and translational movement for certain free radicals. The adsorbent surface, silica gel, is not uniform however, and the effect of this

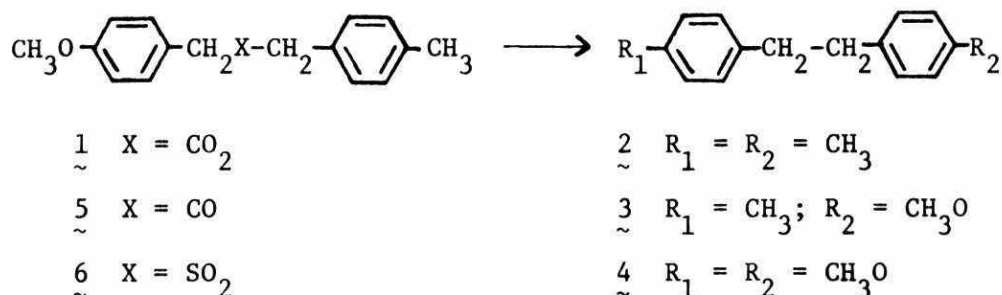
non-uniformity has not been ascertained: the conclusions may be oversimplified. The work to be described demonstrates the occurrence of translational movement unambiguously in different radical systems. The evidence for translational movement in PAH (acenaphthylene, naphthalene derivatives, pyrene) will also be presented.

#### RADICAL PAIR BEHAVIOUR

Our investigation of the behaviour of radical pairs generated from adsorbed organic species was concerned both with the probability of radical movement during the lifetime of the short-lived radical pairs and with the possibility of modification of radical pair behaviour by the surface. Our recent preliminary study (12) has shown that limited translational motion may precede recombination in a singlet radical pair (Photo-Fries rearrangement) generated on dry silica gel. The results to be discussed here indicate that a much greater degree of translational motion is observed for benzyl radical pairs on silica gel. The observation of rotational and translational movement for adsorbed radical pairs produced by azoisobutyronitrile photolysis is also described.

BENZYL RADICAL PAIRS: Photolysis of ester 1 in solution has been shown by Givens (13) to produce a singlet radical pair which, after loss of  $\text{CO}_2$ , gives the three possible bibenzyls 2, 3 and 4. The bibenzyl distribution ranges from 1:2.5:1 (1:2:1 = statistical) in dioxane to 1:5.07:1 in isopropyl alcohol,

thus indicating the presence of a cage effect in the more viscous solvents. Results for the photolysis of 1 on dry silica gel (14) are given in Table 1.



The bibenzyl distribution at 10% monolayer coverage resembles that found in isopropyl alcohol and is not increased at 50% coverage. This indicates, surprisingly, that, at this coverage, molecules of 1 are not interfering with the translational movement of radicals. Such translational motion does decrease at lower temperatures and at  $-50^\circ\text{C}$  the unsymmetrical bibenzyl, 3, derived from geminate pair combination represents ~95% of the bibenzyls.

In contrast with the behaviour of 1, ketone 5, upon photolysis in isopropyl alcohol, gave products 2, 3 and 4 in a 1:2:1 ratio via a triplet radical pair (by analogy with dibenzyl ketone) (15). On dry silica gel (14) the product distribution (Table 1) was closer to statistical than was that obtained from the ester. Cooling to  $-50^\circ\text{C}$  gave a ratio of 1:~6:1 indicating less restriction to movement than with 1. Product ratios comparable to those obtained with 1 at  $-50^\circ\text{C}$  were obtained at  $-165^\circ\text{C}$  for the ketone, 5.

Photolysis of sulfone 6 produces the same bibenzyls, again through a radical pair mechanism. The product distribution for silica gel was similar to that obtained with ester 1, with slightly more geminate pair recombination at room temperature.

The above results lead to the unambiguous conclusion that translational motion on the surface of silica gel can, indeed, compete effectively with radical pair recombination for 1, 5 and 6. The variations in bibenzyl ratio for the formation of the same radicals may be explained by differences in the spin multiplicity of the radical pair. Thus, the singlet pair recombines faster than the triplet and, since the radicals have less time for movement, produces more unsymmetrical geminate recombination product. The similarity between low and high coverage results for a given substrate suggests that the environment of the radicals is much the same at these coverages, i.e., for this system and this coverage range at room temperature, all sites of attachment are effectively equal. "Cage" properties of the silica gel surface are indicated by the increased non-statistical product ratios at lower temperatures.

CYANOPROPYL RADICALS: The solution photolysis of azoisobutyronitrile 7 has been extensively studied (16): loss of nitrogen produces two radicals which couple to produce both 8 and 9 (benzene: 40%, 55%) and disproportionate to give 10 and 11 (~5%). On the other hand, solid state photolysis yields 80-90% of the disproportionation products.

and produce rearranged product, as in solution. This observation is in contrast to reports (18) which claimed that cyanopropyl radicals were anchored to the silica gel surface.

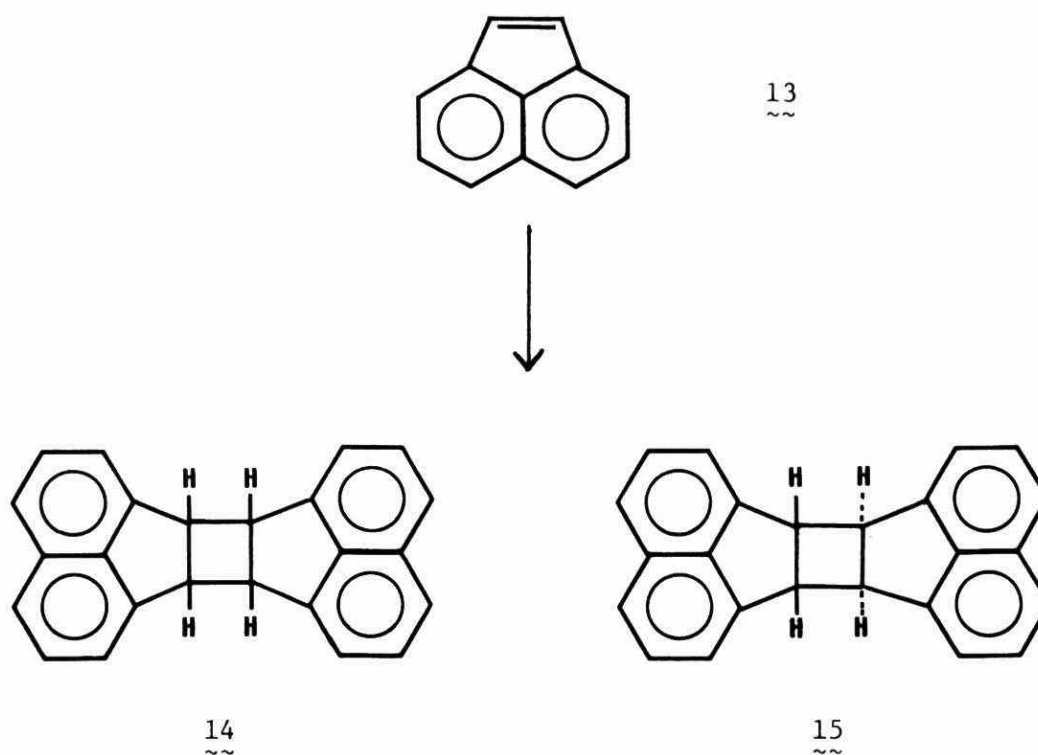
Evidence for translational movement was then sought. Photolysis of mixtures of 7-d<sub>0</sub> and 7-d<sub>12</sub> and deuterium content analysis of the recovered amide (17) showed that significant amounts of amide-d<sub>6</sub> were formed (a typical ratio at 25% coverage was 84.5:17.0:100 for d<sub>0</sub>:d<sub>6</sub>:d<sub>12</sub> amide). The escape of cyanopropyl radicals from the initial geminate pair to form partially deuterated products clearly indicates that translational movement of these radicals does occur. The similarity of surface and solution product ratios and their difference from those in the crystalline phase provide evidence that restrictions on rotational and translational motion on dry silica gel are not severe. We are, thus, led to conclude that, in general, radical migration on a silica gel surface is to be expected.

#### POLYCYCLIC AROMATIC HYDROCARBONS

The investigations discussed in this section were intended to answer two basic questions: (1) Do medium-sized aromatic hydrocarbons migrate on dry silica gel? (2) During the lifetime of a photochemically excited species can translational motion of it, or its ground state equivalent, occur?

DIMERIZATION OF ACENAPHTHYLENE: The irradiation of acenaphthylene 13 in solution produces the cis 14 and trans 15 dimers (19). The singlet has been shown to give only 14 while the triplet gives comparable amounts of both 14 and 15.

Higher cis/trans ratios in the product result with increased acenaphthylene concentration as the encounter probability of singlet and ground state species increases and singlet dimerization competes more effectively with intersystem crossing to the triplet. When 13 adsorbed on dry silica gel was irradiated (20) both dimers were



again formed with the ratio of 14 to 15 varying with coverage as shown in Figure 1. The ratio increases linearly with coverage up to ~15% coverage and above 40% levels off to a value of 21. At the plateau the reaction is shown to be derived 95-97% from the

singlet (from quenching studies). The results suggest that the singlet can only react when it is part of a "nearest neighbour" reactive pair. The longer-lived triplet has, on the other hand, time for migration before reaction.

The dimerization could be sensitized using Rose Bengal, Eosin Y or Acridine Orange at low coverage ( $\sim 0.1\%$ ) with 64.5% coverage for acenaphthylene. As in solution (19) a mixture of  $\sim 14$  and  $\sim 15$  was produced (20). The efficiency observed (at 10% conversion one Rose Bengal molecule sensitized  $>57$  acenaphthylene molecules) cannot be attained with the closest packing possible. Assuming effective energy transfer at  $5 \text{ \AA}$ , less than 20% of the observed dimerization could have occurred. Therefore the results require that translational movement occur, on the time scale of the triplet lifetime, of the monomer in its ground or excited state and of the dimer.

Acenaphthylene dimerization could be quenched by the triplet quencher ferrocene (20). Since the singlet leads essentially to dimer  $\sim 14$ , the slope of the Stern-Volmer plot for quenching of  $\sim 15$  is an indication of the value of  $k_q \tau$ . Assuming that adsorption has little effect on the triplet lifetime of acenaphthylene, the solution value ( $2.5 \mu\text{s}$ ) may be used to obtain a  $k_q$  value of  $7.02 \times 10^{15} (\text{dm})^2 \text{ mol}^{-1} \text{ s}^{-1}$ . This rate constant may be used to show that under these conditions acenaphthylene may move  $\sim 2 \text{ \AA}$  during the singlet lifetime but  $\sim 300 \text{ \AA}$  during the triplet lifetime.



QUENCHING OF PYRENE EMISSION BY HALONAPHTHALENES: Pyrene adsorbed on silica gel shows a nonexponential emission decay (21) which can be described by the rate law  $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . Although  $A_1$ ,  $A_2$ ,  $\tau_1$  and  $\tau_2$  varied from one measurement to another, the mean lifetime,  $\bar{\tau}$ , was constant ( $\pm 0.5\%$ ) during the measurement. A typical  $\bar{\tau}_0$  value was 250 ns. At 0.1% coverage of pyrene, the emission yield,  $\phi$ , and the  $\bar{\tau}$  value were both decreased in the presence of the coadsorbed quenchers, 2-chloro-, 2-bromo-, and 2-iodonaphthalene (20). The Stern Volmer plot for 2-chloronaphthalene is shown in Figure 2. The dependence of  $\bar{\tau}$  on  $[Q]$  and the differing slopes of the  $\phi_0/\phi_q$  and  $\bar{\tau}_0/\bar{\tau}_q$  plots require that static and dynamic quenching processes be operative on the silica gel surface. A comparison of  $k_q$  values in cyclohexane and on silica gel for the three halonaphthalenes (20) leads to the conclusion that on silica gel the quenching rate is diffusion controlled and does not depend on the quencher efficiency as it does in solution. Again, the existence of a dynamic quenching process requires that translational movement occur on the silica gel surface.

#### CONCLUSIONS

The observation of products resulting from nongeminate radical pair recombination following photolysis of ester 1, ketone 5, sulfone 6 and azoisobutyronitrile requires that translational movement occur for adsorbed radicals. Radical

rotational movement is also shown by the observation of the unsymmetrical product 9 from azoisobutyronitrile photolysis. Decreasing the temperature decreases the amount of translational motion, leading to a marked "cage" effect at low temperature.

Translational movement for medium sized polycyclic aromatics has been shown by (a) changes in acenaphthylene dimer composition by irradiation at different surface coverages, (b) sensitization of acenaphthylene dimerization, (c) quenching of acenaphthylene dimerization with ferrocene and (d) Stern-Volmer quenching of pyrene fluorescence by halonaphthalenes. Although it appears that molecules may prefer certain sites on the silica gel surface at room temperature, translational motion still takes place on the timescale of photochemically excited states.

The foregoing demonstrates that bimolecular processes can, in principle, occur between adsorbed molecules and, hence, that the potential for photochemical transformation of adsorbed molecules is far greater than has been heretofore believed. It now remains to be demonstrated what the environmental applicability is. It is not sufficient merely to derive the consequences on the basis of the transformation of individual contaminants, but it will be necessary to consider carefully the consequences of multiple absorbance even at very low coverage since it has now been shown that one is dealing with a dynamic system.

#### ACKNOWLEDGEMENTS

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CAPTIONS

Figure 1. Plot of  $\frac{I_0}{I_\infty}$  against acenaphthylene concentration  
(percentage coverage) on silica gel.

Figure 2. Stern Volmer plots of quenching of pyrene fluorescence  
intensity (o) and lifetime (x) by 2-chloronaphthalene.

Table 1. Photolysis of ester 1, ketone 5 and sulfone 6 on dry silica gel.<sup>a</sup>

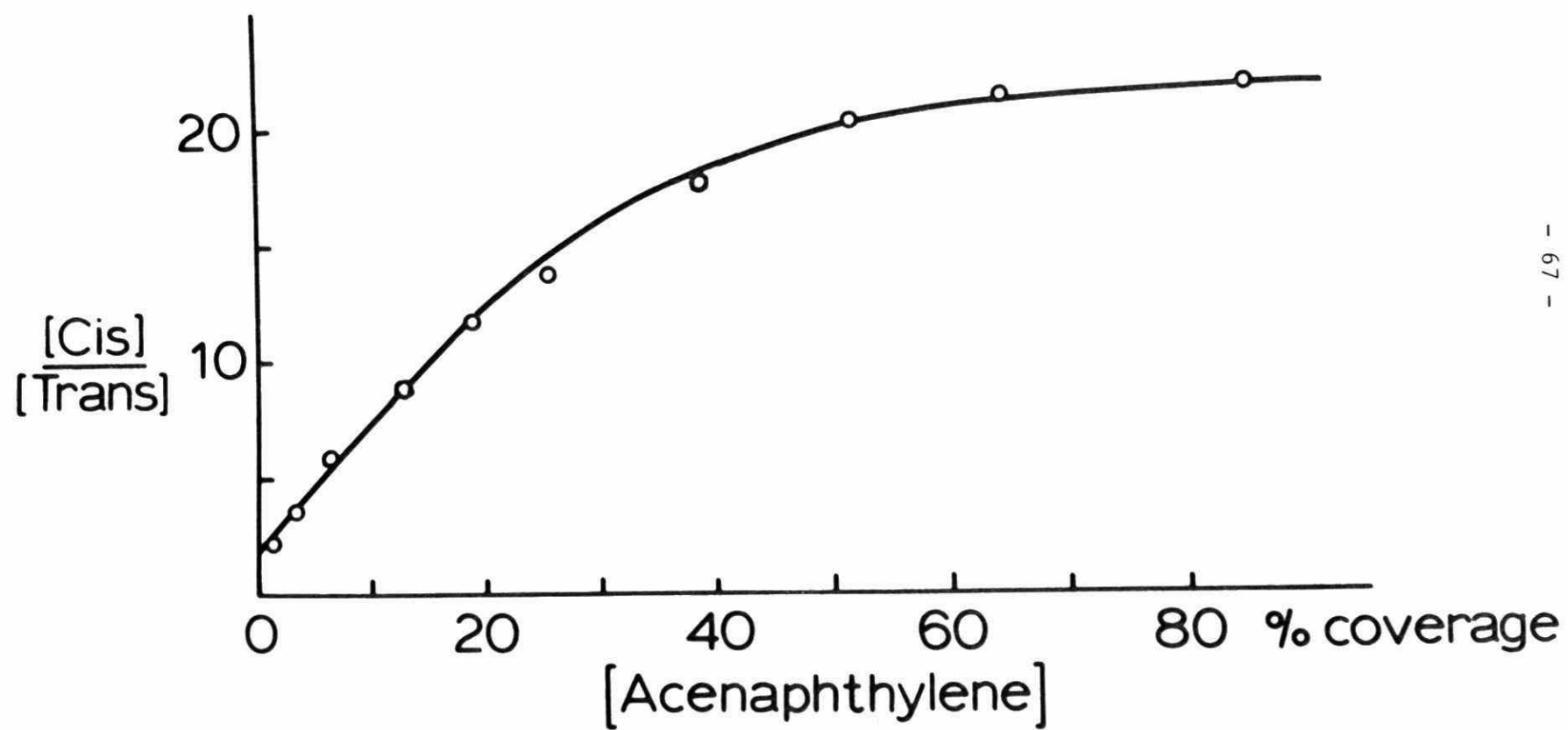
	Coverage <sup>b</sup> (%)	T (°C)	Bibenzyl ratio <sup>c</sup>		
			2	3	4
1	1	20	1.0	6.1	1.0
	10	20	1.4	5.5	1.0
	50	20	1.0	4.1	1.1
	10	-50		>96%	
5	1	20	1.2	3.7	1.0
	10	20	1.0	3.2	1.0
	50	20	1.0	3.1	1.0
	2	-50	1.2	9.0	1.0
	10	-50	1.0	6.3	1.0
	50	-50	1.0	6.2	1.0
	10	-165	trace	>96%	trace
	2	20	1.2	8.3	1.0
6	10	20	1.0	6.2	1.0
	50	20	1.2	6.4	1.0
	10	-50	1.0	30	1.2

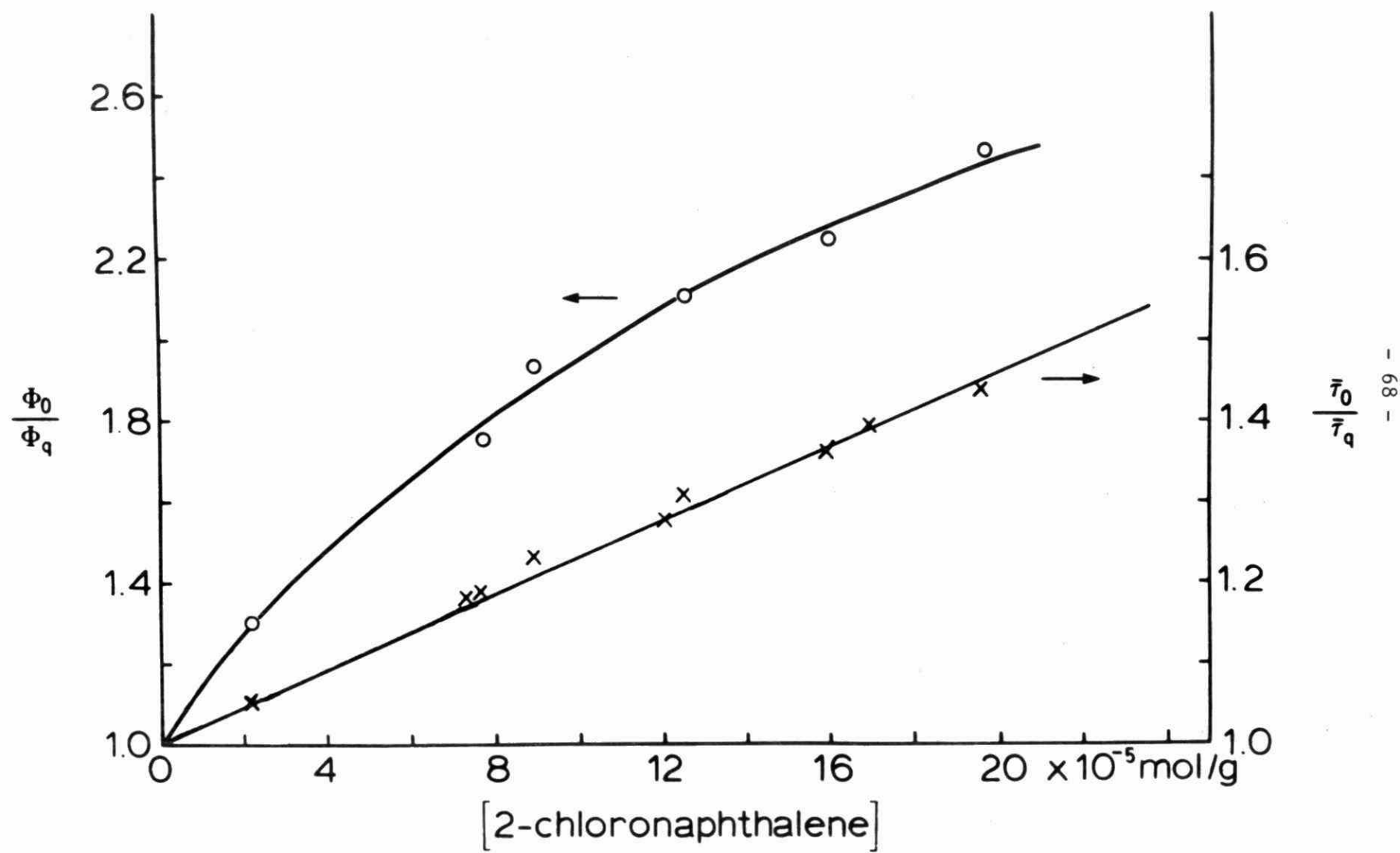
<sup>a</sup>Silica gel (35-70 mesh) was heated to 200°C (0.1 mm Hg) for at least 5 h immediately before use. Samples were degassed to  $<10^{-5}$  mm Hg and irradiated either in vacuo (20°C experiments) or under nitrogen (low temperature experiments) at 254 nm (ester, 20°C) or >220 nm (ketone; ester, -50°C). Sample mixing was accomplished by rotation of the sample tube.

<sup>b</sup>100% monolayer coverage was determined by calculation and from a Langmuir isotherm to be  $\sim 9 \times 10^{-4}$  mole/g silica gel for 1 and 5.

<sup>c</sup>V.p.c. analysis.







MEASUREMENT OF TOTAL ORGANIC CHLORINE  
IN INDUSTRIAL WASTES

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## INTRODUCTION

The wide occurrence of halogenated organics in the environment and their detrimental affect on public health has been well known for sometime. The cost of analysis for specific organic compounds prohibits the analysis of every sample. An analytical method based on Total Organic Halide (TOX) offers a relatively low cost scheme to determine whether or not a sample should be analyzed for specific organics with, most likely, a GC/MS method. Briefly, the TOX method involves the extraction of organics by solvent, adsorption on activated carbon. A portion of the solvent extract is injected into a pyrolysis-oxidation furnace system where the extract is vaporized and the gases oxidized releasing the halogen from the halogenated organic compounds. The activated carbon placed in the furnace is completely burned, thus releasing the halogens. An halide sensitive detector is attached to the furnace outlet, usually a microcoulometer. The TOX method has suffered from a number of serious problems. The primary problem is the separation of  $\mu\text{g/L}$  levels of halo-organings from  $\text{mg/L}$  levels of inorganic chloride present in all samples. The separation techniques can be specific, as shown by solvent, to classes of organics or non specific as carbon adsorption where nearly everything organic or inorganic is adsorbed. The latter case is preferred, however the differentiation of organic halide from the inorganic halide becomes a problem as the microcoulometer, cannot distinguish the organic halide from the inorganic halide. In addition, as the activated carbon is a superb adsorbent, the "virgin" carbon is randomly contaminated and thus the background level is unreliable.

Similarly, solid samples and sludges contain inorganic chloride and it is impossible to eliminate thus the TOX of solids and sludges cannot be determined directly.

This paper presents reliable TOX analytical methods, developed by the authors, applicable to aqueous samples (i.e. drinking water, industrial wastes), solid samples (i.e., soils, ashes), sludges and oils.

# ABSTRACT

Methods to determine the Total Organic Halogen (TOX) content of wide ranging samples has been investigated, improved, developed and applied to aqueous solid and other liquid samples. Aqueous samples were analysed by adsorption on a new activated carbon and pyrolysis and microcoulometry. An average recovery of 94% was obtained for chloro-organics without interference from inorganic chloride. Solvent extraction, rather than direct pyrolysis was required to separate the chloro-organics from solid samples (i.e. soils, ashes) and liquid samples containing high levels of solids (i.e. sludges, slurries). Oil samples were analysed directly.

## EXPERIMENTAL METHODS

### Adsorption System

A 25 mL aliquot of sample, at pH7 was passed at a flow rate of 1 mL/minute, through 2 glass columns (2 mm i.d. and 5 cm long) in series each containing 40 mg adsorbent. The contacting apparatus, shown in Figure 1, was constructed following Dohrmann's (Dohrmann Inc., Santa Clara, CA) AD-2 adsorption module. The exposed carbon in each column was washed in situ with 4 mL of 5%  $\text{NaNO}_3$  solution. The surface water was blown off the carbon in situ with an inert gas. The exposed carbon was forced out of the column into the sample boat. The sample boat then was introduced into furnace section of the Dohrmann MCTS-20 Microcoulometer. The organics were released from the carbon in  $\text{CO}_2$  atmosphere and converted to HCl in a reaction with the  $\text{H}_2$  and  $\text{H}_2\text{O}$  released during oxidation of the released organics. The microcoulometric cell detects chloride introduced as HCl. The signal from the cell was integrated and presented as total ng  $\text{Cl}^-$ .

### Liquid - Liquid Extraction System

A liquid-liquid extractor was constructed based on modification of a system originally suggested by Rhoades and Millar (1965). The apparatus is shown schematically in Figure 2. The extractor was designed to contact a large (up to 1L) volume of water or sludge with a small volume (as low as 0.5 mL) of solvent and to recover a usable (100  $\mu\text{L}$  minimum) portion of the extract for analysis.

To the sample in the flask 50 g  $\text{Na}_2\text{SO}_4$  was added.  $\text{H}_2\text{SO}_4$  was added to lower the pH to 2. After the solvent was added the system was stirred for 30 minutes. Then the extract was forced into the auto sampler vial with saturated  $\text{Na}_2\text{SO}_4$  solution introduced through the side of the flask.

The extracts were analyzed with the Dohrmann MCTS-20 Microcoulometer.

### Solid Extraction System

A ball mill like solid-liquid extractor similar to Solomon's (1979) was used. The schematic diagram is shown in Figure 3. Basically the extractor is a stainless steel tube containing 3 stainless steel ball bearings. Fittings on the ends of the tube facilitate material addition and extract removal. About 15 to 30 grams of solid sample (i.e. soil) along with 7-20 mL solvent are mixed horizontally parallel to the linear movement in an oscillating shaker. After 30 minutes the extract was forced into the auto sampler vial with saturated  $\text{Na}_2\text{SO}_4$  solution introduced at the bottom of the extractor.

The extracts were analyzed with the Dohrmann MCTS-20 Microcoulometer.

### Macrofurnace System

A macrofurnace system was designed and constructed to allow the pyrolysis/oxidation of solid samples weighing upto 5 grams. The system is shown schematically in Figure 4. Briefly the system consists of a quartz tube spanning two furnaces. The first furnace for pyrolysis with programable temperature control and the second furnace for oxidation. The oxidation section of the tube contains platinum wool catalyst. The inlet end of the tube has provisions to introduce sample boat and the outlet end is connected to a fraction collection manifold. Each fraction is collected in specially designed gas scrubber bottles with fitted glass spargers. The bottles were chilled and contained 100 mL of 1% tris (hydroxymethyl) aminomethane buffer to aid condensate recovery. The condensate analyzed with an ultra-sensitive solid state chloride sensitive electrode.

### Belstein Test - Atomic Adsorption System

A burner originally designed by Gutsche (1968) was modified and adopted to the existing carbon rod analyzer head of the Varian Model 6 Atomic Adsorption Spectrophotometer. An indium coated copper foil was placed into the carbon cup. The system was operated as a normal atomic absorption spectrophotometer.

The principle of operation is on based the indium reaction with the evaporated and oxidized chloro-organics and the subsequent evaporation and detection of indium chloride in the flame.

## RESULTS AND DISCUSSION

### Analysis of Drinking Water

Solvent extraction is commonly utilized to separate dissolved organics from water prior to analysis by gas chromatography. Solvents are selectively extract the groups of chemicals competable with the solvent and governed by partition equilibrium. High recovery requires large amounts of solvent resulting in concentrations in the solvent too low to analyse with certainty with the microcoulometer. Evaporation of the solvent with increase the concentration but at the same time, the volatile compounds will be last.

On the other hand, nearly all organic compounds adsorb an activated carbon and all the carbon, thus all the aqueous sample, is used in microcoulometric analysis. This way a complete representative sample is analyzed.

Activated carbon used this way presented three major difficulties that had to be eliminated to make the TOX analysis valid.

First, when the exposed activated carbon was pyrolysed/oxidized the detector produced a random negative signal which, when integrated, subtracted from the total halide detected. A substantial error was thus introduced in the analysis. The cause for the negative signal was traced to the water remaining on the carbon. The water temporarily diluted the electrolyte in the microcoulometric cell upsetting the electrochemical equilibrium. Thus a negative signal was produced until the cell recovered.

The water could not be eliminated from the carbon prior to introduction into the microcoulometric furnace. However, the trap, a miniature gas washing bottle, containing concentrated sulfuric acid place in line between the furnace outlet and the microcoulometric cell successfully stopped the flow of water vapor into the cell. On the other hand, the hydrogen halide produced from the organic halide in the furnace was allowed through as shown by the complete recovery obtained for chlorophenols, chlorobenzenes, chloromethanes, chloroalkanes,



chloroalkenes, PCB's and mirex.

Second, at present the TOX analysis method as represented by EPA's Method 450.1 (interim) (1980) following Takahashi (1979) suffers from gross interferences. Basically, the type of activated carbon and its handling presents a number of inaccuracies.

The activated carbons are usually made from natural materials such as coal. Impurities (both organic and inorganic) from the coal are present on the activated carbon. These impurities will desorb from the carbon according to complex mechanisms involving the carbon surface, the impurities, the organics and inorganics in the sample and the "wash" water and their interactions with the carbon surface and each other. Whatever has been adsorbed on the carbon and what has not desorbed with the "wash" will be released during pyrolysis and if these compounds contain halides, then the halides will be detected.

The contaminants on the inorganic carbon define the blank TOX value and therefore the detection limit of the analysis. This laboratory obtained blank values for the activated when purchased from Dohrmann (Santa Clara, CA.) with an average halogen content of 1032 ng/40 mg of carbon with a standard deviation of 425 ng/40 mg of carbon. If we follow EPA's (1979) criteria for detection limits of 5 times the background noise (the deviation range in the carbon blank can be considered as background noise), then the sample must contribute at least 4250 ng of halide to provide confidence in the analysis. Assuming that a 100 mL sample was passed through the carbon column, then the minimum halide concentration from organic sources must be 42.5 µg/L.

The approach of this laboratory to bring the blank value and thus the detection limit for the TOX analysis into an acceptable range was to find a new adsorbent with a lower level of contaminants and to devise an handling procedure by which the contaminants on the virgin carbon are further reduced.

The activated carbon Zenosorb - 10 (Z-10), reputed to contain low levels of contaminants was obtained from Zenon Environmental Enterprises Ltd., Hamilton. The carbon was crushed and sieved to 100/200 mesh and then soxhlet extracted with water for two days and with acetone

overnight. The carbon then was dried and kept in tightly sealed bottles. The carbon was placed directly in the columns and weighed to minimize contamination from the air.

The blank for Z-10 was evaluated, by washing the carbon with 4 mL of 5%  $\text{NaNO}_3$  solution, at least twice a day when TOX analysis was done. The average of 33 evaluations was 98 ng/40 mg carbon with a standard deviation of 60 ng/40 mg carbon. Thus the detection limit is 4  $\mu\text{g/L}$   $\pm$  50% of organic chloride assuming that 100 mL sample is analyzed. The reproductibility of samples containing organic chloride in excess of 10  $\mu\text{g/L}$  is  $\pm$  25%.

The carbon and procedure described here show a 10 fold improvement in detection limit.

Third, the level of inorganic chloride is expected to range from 0 to 5000 mg/L, while the organic chloride in the 0 to 500  $\mu\text{g/L}$  range. Such high level of inorganic chloride completely blankets the organic chloride as the inorganic chloride also adsorbs on the carbon and thus the organic chloride level is difficult if not impossible to detect.

The EPA (1980) TOX method specifies that the pH of the sample must be during adsorption. At pH 2 with the large excess of  $\text{H}^+$  ions the inorganic chloride in solution associates with  $\text{H}^+$  by ion pairing forming  $\text{HCl}$ .  $\text{HCl}$  adsorbs on the carbon and if in excessive amounts then its removal with the nitrate wash is incomplete and variable. At neutral or slightly basic pH levels the  $\text{H}^+$  ion concentration is greatly reduced and thus the formation of  $\text{HCl}$  is greatly reduced.

The TOX level of a set of model waters was determined by adsorption at pH 7 followed by 4 mL nitrate wash and pyrolysis in the Dohrmann MCTS-20 Microcoulometer. No inorganic chloride was detected in the concentration range of 0 to 5000 mg/L. An average of 94% recovery was obtained for chlorobenzenes, chlorophenols, chloromethanes and chloroalkenes.

The carbon was pyrolyzed only rather than oxidized as pyrolysis alone showed 100% recovery for most compounds, including  $\text{CCl}_4$  and PCB's the most difficult to decompose compounds. The additional oxidation step as specified by EPA (1980), will release the  $\text{NaCl}$

due to the locally high temperatures produced by the burning carbon and thus making the analysis impossible.

### Analysis of Sludges

This laboratory has carried out work on the direct analysis of dried sludge in a macrofurnace system. The condensate was collected and analyzed for  $\text{Cl}^-$  with an ion specific electrode. Sludge was dried to eliminate the uncontrollable, in this case, formation of  $\text{HCl}$  as described earlier.

The municipal return activated sludge contained 4880 mg/L solids and 50.2 mg/L TOX. In addition, the sludge was spiked with hexachlorobenzene and 38% was recovered.

The source of the sludge initial as blank TOX level is both organic and inorganic of unknown composition. Inorganic salts such as  $\text{AlCl}_3$ , posses boiling points below the pyrolysis temperature of  $1000^\circ\text{C}$  thus easily vaporized. The removal of these salts is not possible as the sludge solids are weak adsorbents thus the organics would be lost during the nitrate wash.

The low hexachlorobenzene recovery was caused by the flashing of carbonaceous material in the sludge thus overloading the oxidation section of the furnace resulting in incomplete oxidation and incomplete organic chloride conversion to  $\text{HCl}$ .

The combination of very high and uncontrollable sludge TOX blank value and low organics recovery makes direct analysis of sludges impossible.

Solvent extraction overcomes these problems. Inorganic chloride is not carried over into the solvent. The solvent can extract off the solids and in addition the solids and inorganic salts aid in the extraction by the salt out effect. As the sludge contains high concentration of organics it is not necessary to evaporate the extract to easily detectable levels.

Our extractions with cyclohexane and microcoulometric analysis showed that this sludge contained 68  $\mu\text{g/L}$  organic chloride rather than

50.2 mg/L by direct pyrolysis/oxidation. When the sludge was spiked with chlorinated organics, recoveries of 83% was obtained for mirex, 53% for pentachlorophenol, 80% for hexachlorobenzene and 60% for trichloroethylene. The average recovery of 69% is somewhat low however these compound most likely had adsorbed on the solids in the sludge and their extraction was probably kinetically limited. Trichloroethylene was probably lost by evaporation during handling.

#### Analysis of Soils

The problems associated with the analysis of soils are similar to those associated with sludge. Our determinations with the macrofurnace system showed that 86% of NaCl added to the soil, from aqueous solution, was recovered. The soil was moist and drying it would evaporate some of the organics. This carry over is serious as the inorganic chloride concentration is expected to be substantially higher than the organic chloride concentration and thus the inorganic chloride would blanket the organic chloride.

Soil as a weak absorbent could not be washed with the nitrate solution as the organics would be removed and lost in the process. Therefore soils cannot be directly analyzed for TOX.

Solvent extraction offers a single step separation of organics as small amounts of solvent are required and thus extract concentration is not required due to the high level of organics in soils. This laboratory extracted soils with cyclohexane. The carry over of inorganic chloride was not detected and 88% average recovery was obtained for mirex, pentachlorophenol, and hexachlorobenzene. The soil itself contained 654 ng/g of TOX. A soil, supplied by the Ontario Ministry of the Environment, contaminated by PCB's, contained  $1.7 \pm 0.3$  mg/g of TOX.

#### Analysis of Oils

Samples of dirty crankcase oil spiked with chlorinated organics was

analyzed with the modified Belstein - AA Method and oil contaminated with PCB were analyzed directly with the microcoulometer. Inorganic chloride carry over was not expected and was not observed. In oil without the presence of water the inorganic chlorides exist in the crystalline form and thus could not evaporate, and could not form HCl by ion pairing.

Pentachlorophenol was completely recovered from dirty crankcase oil. The TOX of the PCB contaminated oil, supplied by the Ontario Ministry of the Environment, was  $46 \pm 10$   $\mu\text{g/g}$ . The TOX contributed by the PCB's as Aroclor 1254 was 162 ng/g. The TOX level is 2 orders of magnitude higher than expected from the PCB's and is contributed by the presence of other chlorinated organic compounds in the oil.

### CONCLUSIONS

The following conclusions maybe drawn from this study:

- i) Adsorption on activated carbon is the method for the representative extraction of organics from aqueous samples.
- ii) The interference with microcoulemetric operation can be eliminated by the inline trap.
- iii) Low activated carbon blank for adsorption of organics from aqueous samples can be obtained with Zenosorb-10 and clean up of the carbon prior to use.
- iv) Inorganic chloride interference with the adsorption/microcoulometric analysis of aqueous samples can be eliminated by adsorption at pH 7, a 4 mL nitrate wash and pyrolysis instead of oxidation.
- v) Sludges and soils cannot be analyzed directly and must be extracted with solvent.
- vi) Oils can be analyzed directly.

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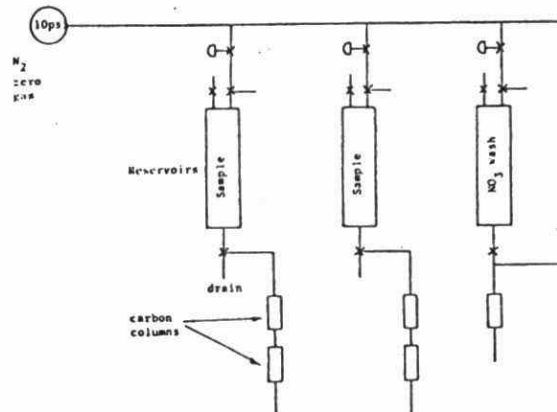
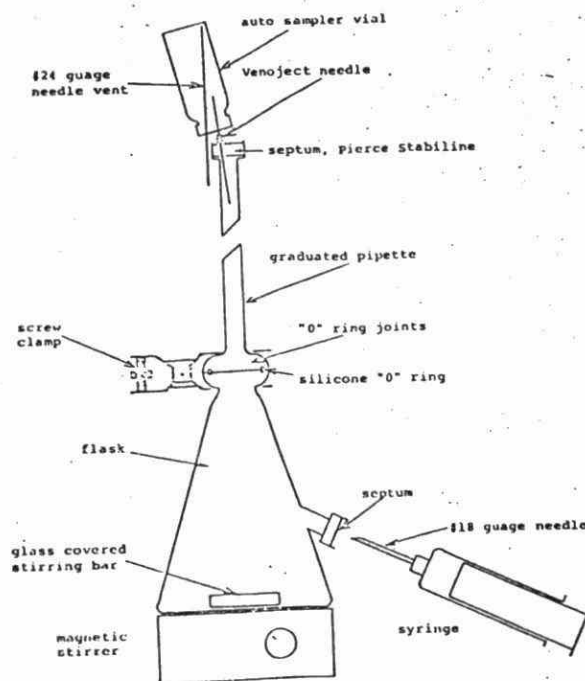


Figure 1. Schematic of the TOX Adsorption Apparatus

FIGURE 2. Schematic of Liquid-Liquid Extractor



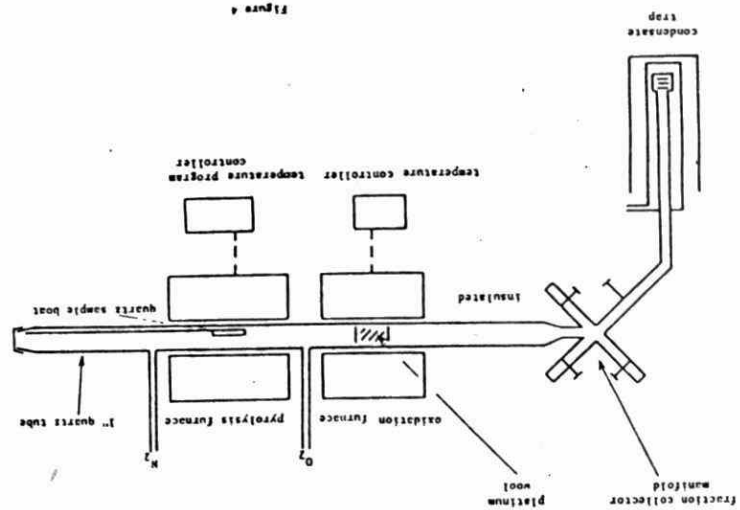


Figure 4  
Schematic of the Microfurnace System

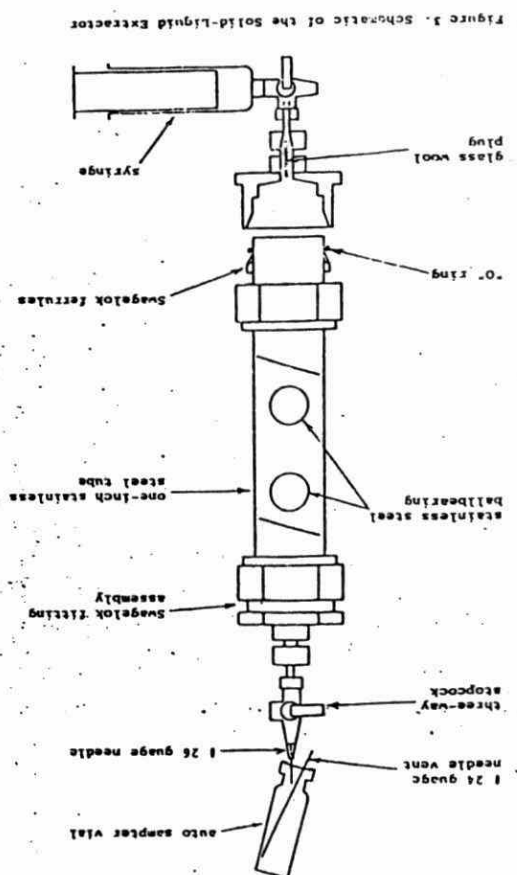


Figure 3. Schematic of the Solid-Liquid Extractor



APPLICATION OF UV DISINFECTION TECHNOLOGY  
IN  
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ABSTRACT

Recent concerns have been raised regarding adverse environmental impacts caused by effluent chlorination and the safety of chlorine handling. This two phase project was initiated to investigate UV light as a cost-effective alternate disinfection technology.

A pilot-scale proprietary UV disinfection unit was transported to eight Ontario WPCP's for disinfection studies. The eight effluents ranged in quality from sand filtered tertiary to poor secondary.

Total coliform (TC) and fecal coliform (FC) target survival densities of 2,000/100 ml and 200/100 ml, respectively, were achieved in all eight plants and both study phases. Corresponding reductions in Pseudomonas aeruginosa (PSA), fecal streptococci (FS) and Escherichia coli (EC) ranged from one to three logs and Salmonella spp. were reduced to <4/100 ml in 80% of the samples. UV transmission appears to be a good surrogate parameter for correlating effluent quality and UV disinfection effectiveness.

After two hours exposure to sunlight at 20°C, photoreactivation was observed in effluent samples that had been inactivated to or below target level TC and FC densities. TC showed approximately two log photoreactivation, whereas EC and FC exhibited one to two logs. Little or no photoreactivation was observed in PSA and FS. After photoreactivation Salmonella spp. densities were estimated to be between 1-10/100 ml.

Photoreactivation was not markedly affected by effluent temperatures between 15°C-20°C; 10 fold dilution of disinfected samples; and reactivation time between 2-24 hours.

## INTRODUCTION

Presently, most water pollution control plants (WPCP's) use chlorine for final effluent disinfection. Unfortunately, chlorination produces some undesirable side effects, such as aquatic toxicity (1), and the formation of potentially hazardous chlorinated organics (2,3). Furthermore, chlorine can be dangerous to transport and handle (4). As a consequence, interest has been stimulated in alternative disinfectants. Many studies have been carried out to evaluate ozone, bromine chloride, chlorine dioxide, gamma ray and ultra-violet (UV) irradiation (5-13). To date, UV irradiation seems to be the most promising alternative. It is competitive in cost with chlorination (14), non-toxic to aquatic life (15) and is relatively safe to handle if direct exposure of skin and eyes is avoided.

Past experience with UV disinfection is, however, limited to high quality secondary and tertiary effluents. There is also a lack of field data regarding the effectiveness of UV irradiation on pathogenic bacteria. Several studies (12,13) have reported that total and fecal coliforms inactivated after UV irradiation, were capable of reactivating when exposed to sunlight. The significance of this phenomenon, known as photoreactivation, upon disinfection effectiveness has yet to be determined. In particular, no parallel comparison of the relative effect of photoreactivation on indicator versus pathogenic bacteria has been conducted.

## OBJECTIVES AND SCOPE

The principal objectives of this project were as follows:

- (1) to establish the UV dosage required to achieve various levels of total and fecal coliform reductions in typical Ontario WPCP effluents;
- (2) to compare the relative reduction and photo-reactivation of selected bacterial organisms to total coliforms;
- (3) to investigate the effect of reactivation time, dilution and effluent temperature on the photo-reactivation of total coliforms.

The study was completed in two phases as outlined in Figure 1. Two tertiary and six secondary WPCP's were studied in Phase 1 and are listed in Table 1. Secondary effluent from the two tertiary WPCP's was also used in this project and therefore provided a total of 10 different WPCP effluents. Four of the eight WPCP's were arbitrarily selected and re-studied in Phase 2. This provided longer term performance data.

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

Figures 2 and 3 provide a schematic description of the proprietary UV disinfection unit and experimental set up, respectively. The UV unit dimensions are approximately 370x770x1400 mm. Twelve G30T8 germicidal lamps and reflectors focus the UV energy into six Teflon tubes containing the liquid to be disinfected. The hydraulic capacity of the unit is rated at approximately 190 l/min (50 US GPM) by the manufacturer.

FIGURE 1 - STUDY OUTLINE

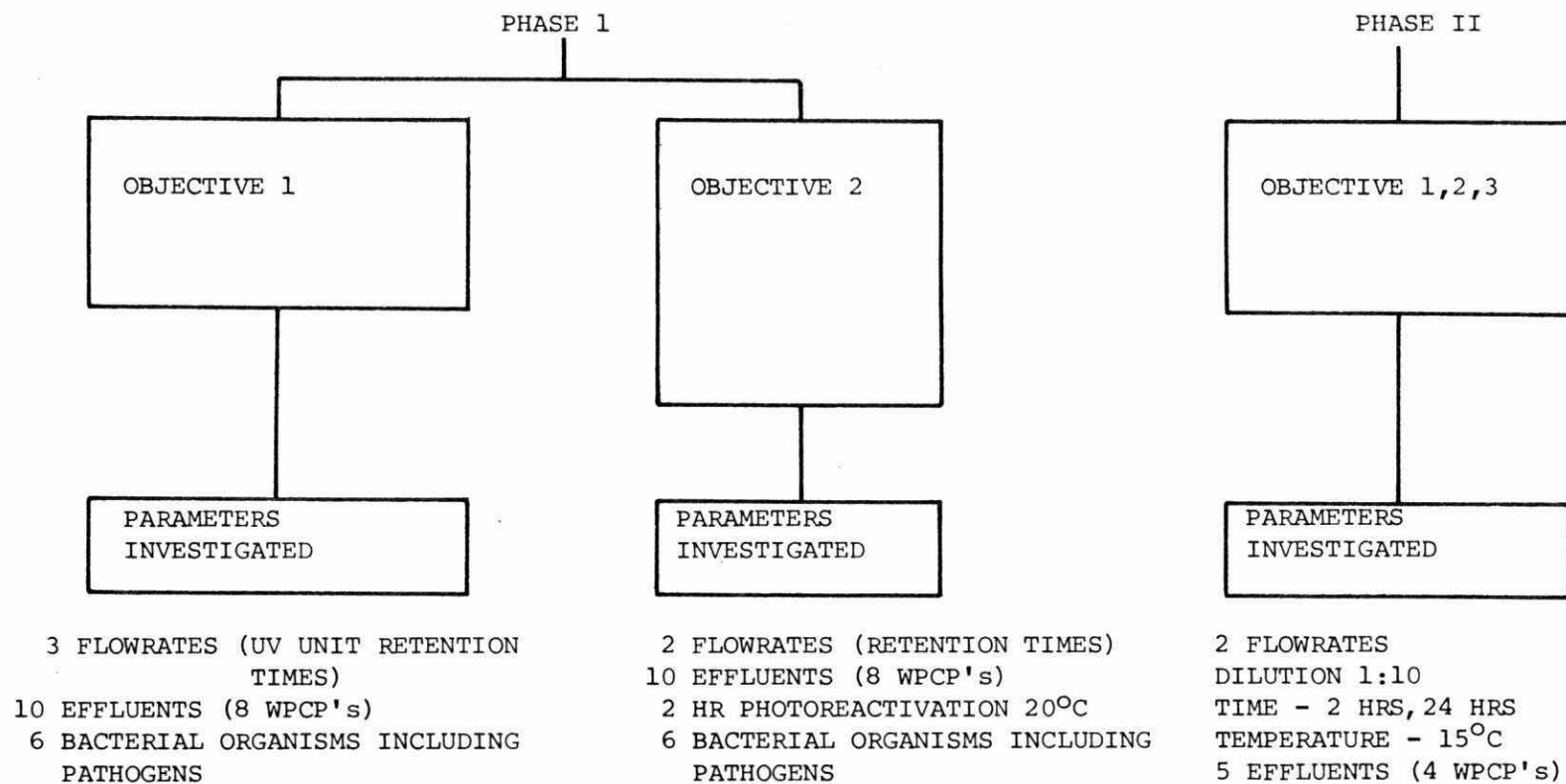


TABLE 1

WPCP EFFLUENTS INVESTIGATED

WPCP	STUDIED IN PHASE 1	STUDIED IN PHASE 2
TORONTO MAIN SECONDARY	X	X
HAMILTON SECONDARY	X	X
BURLINGTON SKYWAY SECONDARY	X	-
TORONTO LAKEVIEW SECONDARY	X	-
TORONTO HUMBER SECONDARY	X	-
GEORGETOWN SECONDARY	X	-
NEWMARKET SECONDARY	X	X
NEWMARKET TERTIARY	X	X
MILTON SECONDARY	X	
MILTON TERTIARY	X	X

NOTE: X INDICATES STUDIED

- INDICATES NOT STUDIED

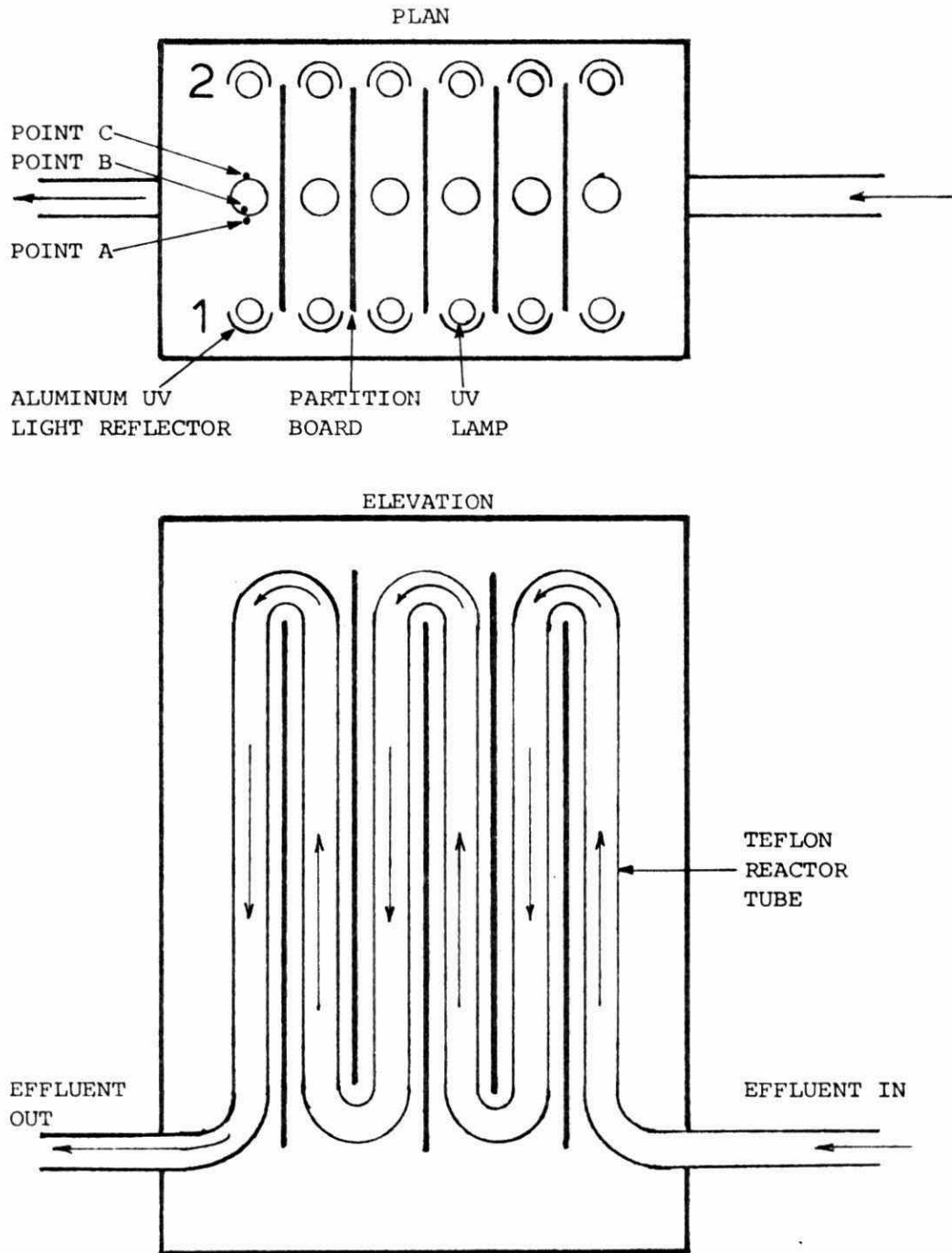


FIGURE 2 - SCHEMATIC DIAGRAM OF UV DISINFECTION UNIT

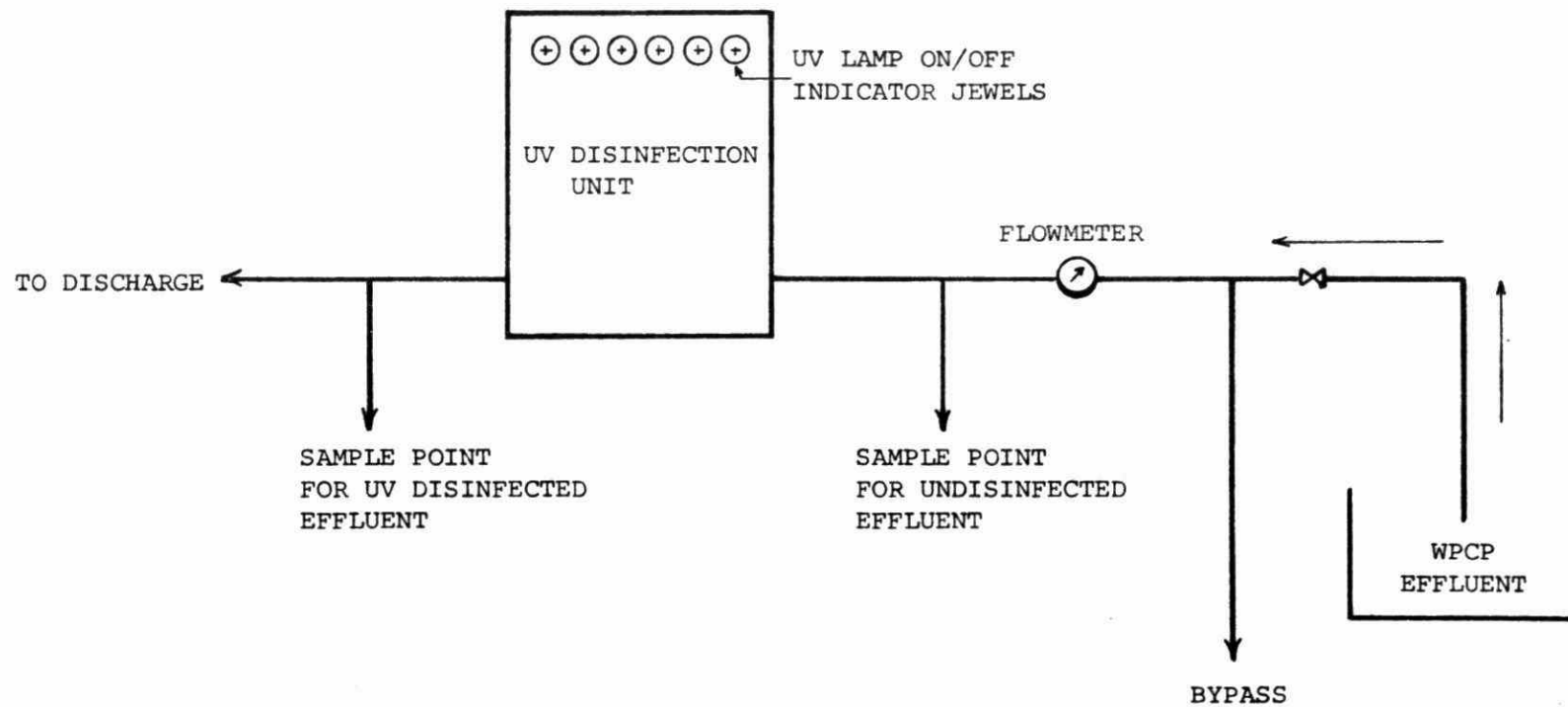


FIGURE 3 - SCHEMATIC DIAGRAM OF EXPERIMENTAL STUDY



The six Teflon reactor tubes were separated from each other by partition boards. This was to prevent UV light leaking to the neighbouring reactor tubes, and complicating dosage estimation. Loss of UV intensity through the Teflon tube was estimated by comparing UV intensities measured at point C (see Figure 2) with UV lamp 2 switched off, and with and without the teflon tube in place. Average UV dosage available within the reactor tube was calculated according to the equation developed by Roeber and Hoot (16):

$$D = 0.6 \times 2 \times I_p \times \left( \frac{1 - e^{-Ad}}{Ad} \right) \times t \text{ (}\mu\text{w-sec/cm}^2\text{)} \quad (1)$$

where  $I_p$  = UV intensity (micro-watt/cm<sup>2</sup>) measured at point A in front of the Teflon tube, and with UV lamp 2 switched off (see Figure 2);

A = sewage effluent absorbance measured at 254 nm wavelength and in a 1 cm cell;

d = film thickness, is taken as the diameter (6 cm) of the reactor tube;

t = true contact time (seconds).

The two constants in equation 1, '0.6 and 2', account for the 40% estimated loss of UV intensity through the Teflon reactor tube, and for two UV lamps irradiating each tube, respectively.

Tracer studies indicated that the UV unit was essentially a 'plug flow' reactor, with negligible back-mixing and shortcircuiting. Hence, true contact time t, could be calculated as 'volumetric flowrate/reactor volume'.

In addition to the effect of effluent absorbance, UV dosage was also systematically varied by adjusting effluent flowrate, hence, nominal contact time through the unit.

Undisinfected effluent samples were obtained three times per day during Phase 1 (start, mid and end of the day), and twice per day during Phase 2 (start and end of the day) for physical/chemical quality analysis. Effluent absorbance and turbidity measurements were performed on site for each run. Samples for bacteriological quality analyses were hand grabbed before and after UV disinfection at the locations indicated in Figure 3. In addition to total coliform (TC) and fecal coliform (FC), Escherichia coli (EC), fecal streptococcus (FS), pseudomonas aeruginosa (PSA) and salmonella spp. (SAL), were also monitored. SAL analyses indicated presence or absence only in 25 ml and/or 100 ml samples. All analyses were performed according to MOE standard methods (17). Bacteriological samples not being used for photoreactivation studies were stored immediately in a dark cooler, at 4°C until analysed. Samples for estimating photoreactivation were held at 20°C in a water bath and exposed to sunlight for 2 hours. Initially, a second sample wrapped in aluminum foil was also placed in the water bath for 2 hours. The second sample was used as 'dark' control for the photoreactivation experiment. The use of 'dark' control sample was discontinued later on in the study because organism reactivation in the dark was not noted.

To study the effect of dilution on photoreactivation in Phase 2, UV disinfected samples were diluted 10 fold with sterilized river water. The magnitude of photoreactivation at 15°C and 2 hours of exposure to sunlight, and at 20°C and 24 hours exposure to sunlight was also studied in Phase 2.

## RESULTS AND DISCUSSION

### WPCP EFFLUENT PHYSICAL/CHEMICAL AND BACTERIOLOGICAL QUALITY

Table 2 shows that physical/chemical quality for the ten effluents was fairly representative of the effluent quality range produced by typical Ontario tertiary and secondary WPCP's. Milton tertiary effluent is noted to be of the highest quality, with low  $BOD_5$ , SS concentrations and high percent UV transmission (percent UV transmission is defined as  $(10^{-\text{absorbance}}) \times 100\%$ ). Toronto Main WPCP produced the lowest and most variable quality final effluent.

Percent UV transmission has been shown to relate well to disinfection efficiency and general effluent quality. With the exception of Milton, Newmarket and Georgetown WPCP effluents, percent UV transmission in the remaining effluents was lower than the average of 65% UV transmission in effluents previously evaluated (9,10,12).

Table 3 is a summary of the bacteriological quality of the ten WPCP effluents. The data indicates that the Humber WPCP effluent contained slightly higher TCu and FCu (total and fecal coliform in undisinfected or final effluent). TCu and FCu in the other nine effluents were within the typical ranges of  $1 \times 10^5$  to  $2 \times 10^6$  TC/100 ml and  $1 \times 10^4$  to  $2 \times 10^5$  FC/100 ml respectively, which are found in many Ontario secondary WPCP effluents prior to disinfection.

TABLE 2 - WPCP EFFLUENT PHYSICAL/CHEMICAL QUALITY

	TORONTO MAIN	HAMILTON	BURLINGTON SKYWAY	TORONTO LAKEVIEW	TORONTO HUMBER	GEORGETOWN
<u>BOD<sub>5</sub></u>						
GM	14.09	6.02	4.82	6.45	8.97	21.21
CV	2.68	1.63	1.26	3.63	1.44	1.36
n	39	33	15	15	15	15
<u>COD</u>						
GM	92.04	39.12	33.87	49.05	41.71	34.84
CV	2.33	1.15	1.56	1.65	1.25	1.19
n	39	33	13	15	15	15
<u>SS</u>						
GM	26.81	12.20	9.20	6.43	11.64	5.85
CV	3.74	1.29	1.13	4.29	1.54	1.26
n	39	33	15	15	15	15
<u>TKN</u> (as N)						
GM	28.62	26.52	2.12	3.87	20.99	14.45
CV	1.44	1.35	1.16	2.17	1.13	1.58
n	39	33	15	15	15	15
<u>TURBIDITY</u>						
GM	6.28	3.17	3.61	3.20	4.13	2.00
CV	2.33	1.77	1.27	3.93	2.68	1.43
n	36	33	15	15	15	15
<u>% UV TRANSMISSION</u>						
GM	34.43	56.80	55.53	51.80	52.91	70.58
CV	1.76	1.13	1.14	1.30	1.10	1.03
n	72	48	30	30	32	30
<u>COLOUR</u>						
GM	54.65	30.66	35.88	37.69	37.94	25.41
CV	1.30	1.27	1.38	1.29	1.14	1.10
n	39	33	15	14	15	15

PG 2

TABLE 2 - WPCP EFFLUENT PHYSICAL/CHEMICAL QUALITY

	NEWMARKET SECONDARY	NEWMARKET TERTIARY	MILTON SECONDARY	MILTON TERTIARY
<u>BOD<sub>5</sub></u>				
GM	13.68	10.76	15.91	2.33
CV	2.36	1.77	2.03	2.12
n	23	27	6	39
<u>COD</u>				
GM	45.87	39.11	38.78	23.18
CV	1.54	1.69	1.17	1.24
n	23	27	6	39
<u>SS</u>				
GM	12.04	4.83	9.11	2.60
CV	2.26	1.74	1.13	1.74
n	21	25	6	39
<u>TKN</u> <u>(as N)</u>				
GM	24.26	22.94	9.24	4.27
CV	1.73	1.28	1.32	1.72
n	23	26	6	39
<u>TURBIDITY</u>				
GM	3.78	1.96	2.04	1.21
CV	2.40	2.08	1.18	2.13
n	23	26	5	39
<u>% UV TRANSMISSION</u>				
GM	56.40	62.85	69.32	76.21
CV	1.30	1.22	1.02	1.02
n	31	41	12	54
<u>COLOUR</u>				
GM	36.98	26.20	21.80	18.03
CV	1.28	1.44	1.22	1.24
n	23	27	5	39

GM = GEOMETRIC MEAN

CV = COEFFICIENT OF VARIATION

n = NUMBER OF DATA ANALYSED

TABLE 3 - BACTERIOLOGICAL QUALITY OF WPCP UNDISINFECTED EFFLUENTS

BACTERIA DENSITY PER 100 ml SAMPLE

		P A R A M E T E R S					NUMBER OF TESTS SHOWING SAL PRESENT
WPCP		TC <sub>u</sub>	FC <sub>u</sub>	EC <sub>u</sub>	FS <sub>u</sub>	PSA <sub>u</sub>	
TORONTO MAIN	*GM	1.3x10 <sup>6</sup>	1.2x10 <sup>5</sup>	1.1x10 <sup>5</sup>	3.3x10 <sup>4</sup>	2.5x10 <sup>3</sup>	** 51/51
	CV	3.22	2.90	3.82	3.07	2.47	
	n	48	36	24	37	48	
HAMILTON	GM	1.3x10 <sup>6</sup>	1.8x10 <sup>5</sup>	3.0x10 <sup>5</sup>	1.5x10 <sup>4</sup>	1.3x10 <sup>3</sup>	52/57
	CV	3.14	4.14	2.11	3.79	3.57	
	n	48	42	30	43	48	
BURLINGTON SKYWAY	GM	1.6x10 <sup>6</sup>	1.4x10 <sup>5</sup>	1.3x10 <sup>5</sup>	1.1x10 <sup>4</sup>	2.7x10 <sup>2</sup>	1/15
	CV	1.79	1.56	1.64	1.78	9.31	
	n	16	15	15	15	15	
TORONTO LAKEVIEW	GM	1.6x10 <sup>5</sup>	1.4x10 <sup>4</sup>	1.2x10 <sup>4</sup>	2.5x10 <sup>3</sup>	8.0x10 <sup>1</sup>	7/15
	CV	4.15	5.18	5.93	5.97	3.79	
	n	15	15	15	15	15	
TORONTO HUMBER	GM	3.4x10 <sup>6</sup>	2.4x10 <sup>5</sup>	2.2x10 <sup>5</sup>	3.3x10 <sup>4</sup>	2.0x10 <sup>3</sup>	13/16
	CV	1.52	1.60	1.60	1.76	1.75	
	n	16	16	16	16	16	
GEORGE- TOWN	GM	7.7x10 <sup>4</sup>	9.2x10 <sup>3</sup>	8.3x10 <sup>3</sup>	3.5x10 <sup>3</sup>	2.9x10 <sup>1</sup>	0/20
	CV	1.65	1.78	1.84	1.46	1.83	
	n	15	15	15	15	15	

TABLE 3 - BACTERIOLOGICAL QUALITY OF WPCP UNDISINFECTED EFFLUENTS

BACTERIA DENSITY PER 100 ml SAMPLE

WPCP		TC <sub>u</sub>	FC <sub>u</sub>	EC <sub>u</sub>	FS <sub>u</sub>	PSA <sub>u</sub>	NUMBER OF TESTS SHOWING SAL PRESENT
NEWMARKET SECONDARY	GM	$7.3 \times 10^5$	$1.1 \times 10^5$	$7.4 \times 10^4$	$3.2 \times 10^4$	$9.7 \times 10^2$	25/36
	CV	3.14	3.09	2.78	2.17	3.23	
	n	21	15	11	15	21	
NEWMARKET TERTIARY	GM	$6.1 \times 10^5$	$9.7 \times 10^4$	$5.3 \times 10^4$	$2.0 \times 10^4$	$1.0 \times 10^3$	32/45
	CV	5.04	4.20	2.60	3.19	5.29	
	n	24	24	16	24	24	
MILTON SECONDARY	GM	$1.4 \times 10^5$	$2.3 \times 10^4$	$2.2 \times 10^4$	$1.9 \times 10^3$	$1.4 \times 10^2$	2/7
	CV	1.45	1.13	1.15	1.50	1.36	
	n	6	6	6	6	6	
MILTON TERTIARY	GM	$7.7 \times 10^4$	$1.3 \times 10^4$	$6.6 \times 10^3$	$8.2 \times 10^2$	$4.0 \times 10^1$	8/51
	CV	2.12	1.70	1.36	2.17	1.53	
	n	39	33	15	33	39	

NOTE: - \* GM = GEOMETRIC MEAN (COUNTS/100 ml)

CV = COEFFICIENT OF VARIATION

n = NUMBER OF DATA

\*\* = THE NUMBER RIGHT OF SLASH REFERS TO THE NUMBER OF TESTS PERFORMED

#### EFFECTIVENESS OF UV DISINFECTION

Initially log (TCr) vs UV dosage data for each specific effluent was plotted and analysed. Although all effluent data could not be accommodated by one curve, the relationship between log TCr and UV dosage was consistent for all effluents and can best be represented by an inverse equation of the following form:

$$\log (\text{TCr}) = A + B/D \quad (2)$$

where A and B are constants determined from  
experimental data

D - applied UV dosage

TCr - total coliform density after disinfection.

Three curves resulting in three data groupings were required to best describe all the log TCr vs UV dosage effluent data, and are as follows:

$$\text{Group 1} \quad \log (\text{TCr}) = 0.05 + 55533/D \quad (3)$$

$$\text{Group 2} \quad \log (\text{TCr}) = 1.82 + 30631/D \quad (4)$$

$$\text{Group 3} \quad \log (\text{TCr}) = 3.01 + 22478/D \quad (5)$$

Since three equations are required to represent all the data, this suggests that UV absorbance of the effluent may not completely account for all effluent quality variation.

The three data groups and their respective 'best fit' curves are presented in Figures 4 to 6. Figure 4 shows that UV disinfection is the most effective on the two tertiary effluents (group 1). A similar observation was reported by Severin (11) and Johnson (13). It is evident that 10 TCr/100 ml is readily achievable in a high quality tertiary effluent. Table 4 provides the required UV dosage to achieve the target levels of 250 and 2,500 TCr/100 ml. The higher UV disinfection effectiveness in tertiary effluent is attributed to shearing of activated sludge solids by filtration and some actual removal of solids clumps which may hide bacteria. The solids shearing allows more direct exposure of bacteria to UV irradiation.



FIGURE 4 - EFFECTIVENESS OF UV DISINFECTION IN TERTIARY EFFLUENTS, NEWMARKET (8), MILTON (2)

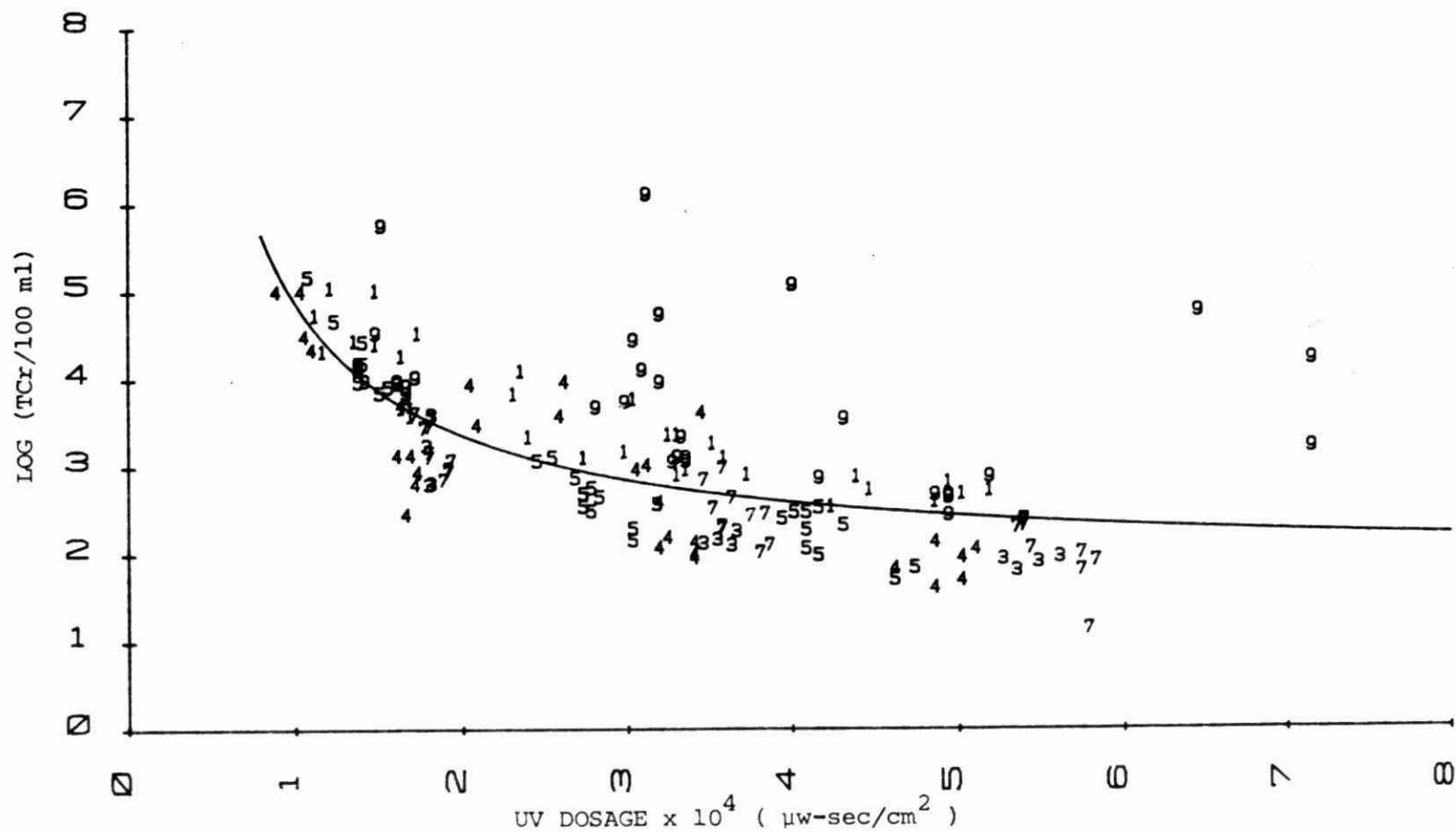


FIGURE 5 - EFFECTIVENESS OF UV DISINFECTION IN SECONDARY EFFLUENTS, NEWMARKET (9), MILTON (3), BURLINGTON (1), LAKEVIEW (4), HUMBER (5), GEORGETOWN (7)

FIGURE 6 - EFFECTIVENESS OF UV DISINFECTION IN SECONDARY EFFLUENTS, HAMILTON (0), MAIN (6)

TABLE 4

ESTIMATED UV DOSAGES REQUIRED TO

ACHIEVE 250 TCr/100 ml AND 2,500 TCr/100 ml

WPCP EFFLUENT GROUPS	UV DOSAGE ( $\mu\text{w-sec/cm}^2$ ) FOR	
	250 TCr/100 ml	2,500 TCr/100 ml
<hr/>		
<u>GROUP 1</u> TERTIARY EFFLUENTS FROM NEWMARKET AND MILTON WPCP's	24,000	17,000
<u>GROUP 2</u> SECONDARY EFFLUENTS FROM NEWMARKET MILTON BURLINGTON LAKEVIEW GEORGETOWN HUMBER WPCP's	53,000	19,000
<u>GROUP 3</u> SECONDARY EFFLUENTS FROM TORONTO MAIN AND HAMILTON WPCP's	--	58,000

NOTE: UV DOSAGE IS ROUNDED OFF TO 2 SIGNIFICANT FIGURES

The few outlying data on Figure 4 represent disinfection of Newmarket tertiary effluent during activated sludge process upset conditions. As noted in equation 1, a factor accounting for UV effluent absorbance is included in the calculation of applied dosage. Accordingly, outlying data again implies that the absorbance factor may not sufficiently account for the full effect of effluent quality fluctuation on UV disinfection efficiency, particularly under these upset conditions.

The group 2 effluent data are presented in Figure 5. The outlying Newmarket secondary effluent data are again noted. A comparison of Figure 4 and 5 shows that to reduce TCr from 2,500/100 ml to 250/100 ml in group 1, effluent requires an approximate 1.4 times dosage increase, whereas group 2 effluent requires nearly 3 times more dosage. The required UV dosage for disinfection to target level is supplied in Table 4.

There are two additional points to be noted in Figure 5. First the lowest achievable TCr was about 200/100 ml, and secondly the higher TCu in the Humber WPCP effluent did not affect the relationship between TCr and UV dosage (see also Table 3).

Until further data analyses are completed, it is uncertain what other factors in addition to effluent absorbance caused UV disinfection to be the least effective in group 3 effluent (Hamilton and Toronto Main WPCP's) shown in Figure 6. A preliminary examination of Table 2 and 3 revealed that while Toronto Main WPCP effluent was marginally poorer in quality, no clear distinction in quality can be drawn between Hamilton and the remaining six secondary effluents (group 2 effluents). In this study, 250 TCr/100 ml could not be achieved by UV irradiation in Hamilton and Toronto Main WPCP effluents as shown in Figure 6.

Analysis of  $\log TCr/TCu$  (TC remaining after disinfection/ TC present before disinfection) vs UV dosage also proved to be best represented by equation 2 and resulted in the same effluent groupings. These plots do not add significantly to this discussion and are therefore not presented. It should be noted that equations 3,4,5 are applicable only within the experimental conditions observed in this study.

The relationships between FCr and UV dosage approximated the relationships between TCr and UV dosage, hence no Figures are presented.

The UV disinfection efficiency of all organisms investigated in this project is related and assessed in terms of total coliform bacteria remaining after disinfection (TCr), (i.e. organism density when TCr is within certain limits). This approach was followed because the reduction of selected organisms relative to total coliform was not affected by effluent quality.

Reduction of FC, EC, FS, PSA and SAL achieved in the ten UV disinfected effluents is summarized in Tables 5 and 6 for specified ranges of TCr. By comparing Tables 3, 4 and 5, it can be concluded that UV irradiation inactivated FC, EC, FS, as effectively as it inactivated TC. At 1,000-5,000 TCr/100 ml, PSA was reduced to near its lowest detectable limit of 4 organisms/100 ml (laboratory analysis limit). At the same TCr range, 81% of the samples (35 of 43 data) show SAL was reduced to <4/100 ml.

TABLE 5 - RESIDUAL BACTERIAL DENSITIES AFTER UV DISINFECTION

	FCr/100 ml		ECr /100 ml		FSr/100 ml		PSAr/100 ml	
	A	B	A	B	A	B	A	B
GM	$4.2 \times 10^1$	$3.3 \times 10^2$	$3.7 \times 10^1$	$2.0 \times 10^2$	$8.3 \times 10^1$	$4.7 \times 10^2$	4	5
CV	2.21	2.21	2.28	2.91	2.34	2.65	1.37	1.53
n	71	77	69	71	69	78	69	84

NOTES: - COLUMN A FOR TCr IN THE RANGE OF 100-500 TC/100 ml  
 COLUMN B FOR TCr IN THE RANGE OF 1,000-5,000 TC/100 ml

TABLE 6

SAL DETECTIONS AFTER UV DISINFECTION

RANGES OF TCr/100 ml					
	<100	>100- <500	>500- <1,000	>1,000- <5,000	>5,000- <10,000
% FREQUENCY, SAL <4 PER 100 ml SAMPLE	100%	95%	94%	81%	73%
NO. OF DATA	14	19	16	43	22



PHOTOREACTIVATION OF TC AND OTHER SELECTED  
BACTERIAL ORGANISMS

The magnitude of photoreactivation effects for TC, FC, FS and PSA are presented in Table 7. The geometric mean densities of the above organisms after photoreactivation are summarized in Table 8. Table 7 shows that a very high degree of photoreactivation of TC, FC and EC occurred during the study. The 1.4 to 1.7 orders of TC photoreactivation are higher than values obtained under comparable conditions in the US (12,13). The US work determined an increase of only one order of magnitude after photoreactivation. No reasons are apparent for the difference at this time.

Significantly smaller increases in pathogenic organisms were observed after photoreactivation, according to Table 7. In fact, FS did not photoreactivate whatsoever. Although some reactivation was observed, the magnitude of photoreactivation of PSA is small and therefore, felt not to be important. Only data that showed SAL present before UV disinfection and subsequently absent after UV disinfection, were included in the SAL photoreactivation data analysis. Table 9 illustrates that SAL can photoreactivate. The likelihood for photoreactivation to occur increased as TCr increased. Unfortunately, the significance of SAL photoreactivation is difficult to assess because the test was non-quantitative. The positive recovery of SAL determined by this study can be the result of one or more SAL in a 25 or 100 ml sample. It is felt that the data of Table 9 probably over states the significance of SAL photoreactivation. It will be shown in the next section that SAL density did not increase significantly after photoreactivation.

TABLE 7 - THE MAGNITUDE OF PHOTOREACTIVATION OF  
ORGANISMS AT SELECTED TCr RANGES

	log TCp/TCr		log FCp/FCr		log ECp/ECr		log FSp/FSr		log PSAp/PSAr	
	A	B	A	B	A	B	A	B	A	B
GM	1.71	1.41	1.30	1.15	1.25	1.39	.07	-.10	.22	.62
CV	.28	.35	.23	.48	.27	.37	.20	.36	.30	.35
n	39	45	37	38	34	18	37	38	38	45

NOTE - COLUMN A FOR 100-500 TCr/100 ml RANGE  
COLUMN B FOR 1,000-5,000 TCr/100 ml RANGE

TABLE 8 - MEAN DENSITIES OF BACTERIAL ORGANISMS MEASURED  
AFTER 2 HOURS OF PHOTOREACTIVATION AT SELECTED TCr RANGES

	TCp/100 ml		FCp/100 ml		ECp/100 ml		FSp/100 ml		PSAp/100 ml	
	A	B	A	B	A	B	A	B	A	B
GM	$2.3 \times 10^4$	$4.0 \times 10^5$	$8.4 \times 10^2$	$3.8 \times 10^3$	$6.4 \times 10^2$	$6.4 \times 10^3$	$1.0 \times 10^2$	$2.7 \times 10^2$	8	18
CV	2.22	2.38	2.17	3.71	2.21	2.70	1.93	2.88	2.12	2.38
n	39	45	39	45	34	18	39	45	39	45

NOTE - COLUMN A FOR 100-500 TCr/100 ml RANGE  
COLUMN B FOR 1,000-5,000 TCr/100 ml RANGE

TABLE 9

PHOTOREACTIVATION OF SAL

-----					
RANGES OF TCr/100 ml					
-----					
	<100	>100- <500	>500- <1,000	>1,000- <5,000	>5,000- <10,000
-----					
% FREQUENCY OF SAL PHOTO- REACTIVATION	0%	65%	40%	55%	83%
# OF DATA	3	15	15	29	16
-----					

#### FACTORS AFFECTING PHOTOREACTIVATION

Table 10 demonstrates the effects of sample dilution, reactivation time, and effluent temperature on TC photoreactivation. These effects were determined by paired data analysis. The average of the paired data differences for each effect (dilution, temperature, etc) was calculated and tested at the 95% confidence level using the paired student -t test.

Column 1 shows that TC photoreactivation stabilized after 2 hours of exposure to sunlight. As a result, the mean difference between the magnitude of photoreactivation measured after 2 hours and after 24 hours was proved to be insignificant according to the 'paired student -t test'. This suggests that the major portion of photoreactivation will occur during the first two hours of exposure to sunlight. Since dilution is available in most receiving streams, the effect of diluting the UV disinfected effluent on photoreactivation was investigated. Results in Table 10 show that the magnitude of TC photoreactivation was about half an order lower in the 10 fold diluted samples. However, after 24 hours reactivation time, the magnitude of photoreactivation in diluted samples was the same as in undiluted samples.

The last column of Table 10 shows that TC photoreactivation was not affected by a 5°C difference in effluent temperature. The two temperatures 15°C and 20°C are typical of stream temperatures in Southern Ontario between late spring and late fall.

Photoreactivation of SAL in diluted samples was also investigated and the data is shown in Table 11. Comparing the photoreactivation results in the 10 fold diluted samples to those of the undiluted samples, on most occasions the number of SAL after photoreactivation was probably in the range of 1/100 ml to 10/100 ml.

TABLE 10

COMPARISON OF THE MAGNITUDES OF TC  
PHOTOREACTIVATION OBTAINED UNDER SELECTED CONDITIONS

	$U_2 - U_{24}$	$U_2 - D_2$	$U_{24} - D_{24}$	$D_2 - D_2$
A. MEAN	.11	.47	-.18	-.02
STD. DEV.	.87	.39	.33	.07
PAIRS OF DATA COMPARED	77	77	77	29

NOTES: -  $U_2, U_{24}$  = MAGNITUDE OF TC PHOTOREACTIVATION  
'LOG (TC<sub>p</sub>/TC<sub>r</sub>)' IN UNDILUTED SAMPLES  
AT 20°C AND AFTER 2 HOURS AND 24 HOURS  
OF REACTIVATION, RESPECTIVELY.

-  $D_2, D_{24}$  = MAGNITUDE OF TC PHOTOREACTIVATION  
'LOG (TC<sub>p</sub>/TC<sub>r</sub>)' IN 10 FOLD DILUTED  
SAMPLES AT 20°C, AND AFTER 2 HOURS  
AND 24 HOURS REACTIVATION, RESPECTIVELY.

$D_2$  = MAGNITUDE OF TC PHOTOREACTIVATION  
'LOG (TC<sub>p</sub>/TC<sub>r</sub>)' IN DILUTED SAMPLES,  
AFTER 2 HOURS OF REACTIVATION, AND AT  
15°C.

TABLE 11

PHOTOREACTIVATION OF SAL

10 FOLD DILUTED SAMPLES

	TCr 100-<1,000	TCr >1,000-5,000
% PHOTOREACTIVATION	0%	17%
# OF DATA	10	18

THE APPLICABILITY OF UV DISINFECTION IN ONTARIO WPCP'S

The ultimate purpose of effluent disinfection is to reduce pathogenic bacteria such that downstream users will be adequately protected from water borne diseases. As a result, the following bacteriological quality:

".....The guideline limit (geometric mean of a series of samples) and upper limit for total coliforms will be 2,500 TC/100 ml and 5,000 TC/100 ml, respectively. The guideline limit for fecal coliforms will be 200 FC/100 ml....."

has been proposed for chlorinated secondary effluents in Ontario (17). Results developed by this study clearly show that UV disinfection can readily achieve the proposed bacteriological quality in most Ontario secondary WPCP's. PSA and SAL the two most commonly occurring pathogens in sewage effluent will also be effectively reduced when the proposed quality is achieved. Unfortunately, both PSA and SAL exhibited a small degree of photoreactivation. The implications on human and animal health, especially in receiving streams with little or no dilution are not immediately known. At this stage, the appropriate health officers should be consulted prior to replacing chlorination with UV light.

TC and FC are poor indicators of potential pathogen contamination because they exhibit a much higher degree of photoreactivation than PSA and SAL. Furthermore, high TC and FC densities downstream from a WPCP using UV disinfection can be due to photoreactivation and/or additional non-point source contamination. Since FS does not photoreactivate, this organism group would be an ideal indicator of receiving stream water quality. Enterococcus which is part of the FS group has been shown to correlate well with gastroenteritis which is a common illness among swimmers (18,19).

The cost of UV disinfection has been projected by several studies (11,12,13) to be competitive with chlorination in WPCP's up to 45,400 m<sup>3</sup>/day capacity. It is competitive with chlorination/dechlorination in larger WPCP's.



## CONCLUSIONS

The study data and conclusions can be summarized as follows:

- (1) UV disinfection is a cost effective alternative to chlorine and would be applicable to most Ontario secondary WPCP effluents.
  - The UV dosages required to achieve 2,500 TCr/100 ml in the effluents studied were 17,000, 19,000 and 58,000  $\mu\text{W}\cdot\text{sec}/\text{cm}^2$  for group 1 (two tertiary effluents), group 2 (six secondary effluents), and group 3 (Toronto Main and Hamilton secondary effluents), respectively;
  - The lowest achievable TCr densities in effluent groups 1, 2 and 3 were approximately 10, 200 and 2,000 TCr/100 ml, respectively.
- (2) UV disinfection is as effective in reducing the selected organisms (EC, FS, PSA, SAL) as in the reducing total coliforms.
  - At the proposed effluent target levels of 2,500 TC/100 ml and/or 200 FC/100 ml, FSr, ECr, and PSAr densities were approximately 470, 200, and 5 per 100 ml, respectively;
  - SAL was reduced to <4 organisms per 100 ml sample, 80% of the time.
- (3) Indicator organisms exhibited significantly higher photoreactivation than the pathogens.
  - At 20°C and 2 hours exposure to sunlight, TC, FC and EC exhibited 1.4 to 1.7 logs of photoreactivation;
  - SAL densities were estimated to be in the range of 4 to 10 organisms per 100 ml. PSA showed about half an order of photoreactivation and FS did not photo-reactivate under the same conditions.

- (4) Temperatures of 15°C and 20°C as well as 2 and 24 hour reactivation times did not appreciably affect photo-  
reactivation.
  - ten fold dilution of disinfected effluent samples exhibited one half order less photoreactivation than non-diluted samples.
- (5) UV absorbance appears to correlate well with disinfection efficiency or TCr, under normal WPCP operating conditions.
  - however, it does not appear to be the sole parameter affecting disinfection according to WPCP 'upset' conditions.

RECOMMENDATIONS

The following recommendations are offered for consideration in future studies of UV disinfection of WPCP effluent:

- (1) Quantitative analysis of SAL photoreactivation should be carried out.
- (2) Photoreactivation studies under actual receiving water dilution conditions may be beneficial.
- (3) The effect of effluent particle size on UV disinfection should be determined.

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GROUNDWATER MOUNDING UNDER A LARGE LEACHING BED

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ABSTRACT

The fluctuations of the water table beneath a large experimental leaching bed, 84 m long and 64 m wide, were monitored for about 2-1/2 years. Field measurements were compared with theoretical results calculated by two mathematical models proposed by Hantush and Sykes, and the limitations of the models for the prediction of the magnitude of mounding were discussed. The factors affecting the movement of the water table were studied and design guidelines pertaining to groundwater mounding were suggested on the basis of this field experience.

## INTRODUCTION

Large leaching beds have been used for on-site disposal of sewage effluent from subdivision developments, shopping centres, motels, etc. One of the main considerations in the design of a leaching bed is the mounding of the water table beneath the bed. If the mounding is excessive, the effluent would be ponded on the ground surface and the contaminants would be transported by the surface runoff. Since limited field data were available on the performance of large leaching beds, there was a need to study the performance of such a system under actual field conditions.

In 1976, a project was initiated by the Applied Sciences Section of the Ontario Ministry of the Environment to study the environmental impact of a large leaching bed system. One of the objectives of the study was to determine the effect of hydraulic loading on the water table beneath the bed. Fluctuations in the ground water level were collected during a 146-week study period. Two mathematical models were used to obtain theoretical results which were compared with the experimental data. From this relatively long-term monitoring program, a good understanding of the factors controlling the ground water mounding beneath a large leaching bed was obtained.

## SITE AND EXPERIMENTAL SYSTEM

A test site adjoining the Norwood Sewage Treatment Plant was used for the construction of the experimental system. Norwood is situated in central Ontario, 27 km east of the City of Peterborough. The design capacity of the plant was 730,000 L/day with an effluent low in biochemical oxygen demand and suspended solids and high in nitrates, typical of a small package plant.

The experimental system used in this study was comprised mainly of:

- (1) A feed tank and a double loop syphon system capable of feeding a known quantity of sewage effluent to the leaching bed.
- (2) A concrete distribution box to distribute the flow to all sections of the leaching bed.
- (3) A leaching bed, 84 m by 64 m in size, made up of 2,440 metres of trenched perforated pipes for spreading sewage effluent into the soil.

In Figure 1, the feed tank, the distribution box and the leaching bed are shown.

The topography at the leaching bed location was quite flat with a difference of only 0.5 m in elevation between the north part and the south part of the bed. Generally the ground dipped towards Ouse River and also sloped slightly in the north-east direction.



The soil stratigraphy at the test site was determined by soil borings at a number of locations and by performing laboratory tests on soil samples. In addition, the location of the bedrock was measured by resistivity and seismic techniques. It was found that the site was underlain by a layer of silty sand to sandy silt overlying a layer of clayey silt on limestone bedrock, which sloped towards Ouse River. Figure 2 shows a soil stratigraphy through the north-south centreline of the leaching bed. On the south side of the leaching bed, a dense layer of silt with sand and gravel was found at approximately 4 to 5 m below the ground surface.

The elevation of the water table, before subsurface disposal, was established by measuring the depth of the ground water level in the piezometers from the ground surface. Figure 1 shows the initial water table contours and the locations of the piezometers. The bottom perforated sections of the piezometers were generally about 1.0 m below the water table.

These contours indicate the presence of a slight water table mounding below the leaching bed prior to the field testing program. On the south side of the bed, a slight depression of the water table was noted. This anomaly could have been due to the presence of a layer of sand, gravel and clayey silt mixture and a probable downward flow of ground water at this general location.

#### WATER TABLE FLUCTUATIONS

Typical water table fluctuations are presented in Figure 3. Two groups of results are presented: one from piezometers installed within the leaching bed and the other from piezometers installed at varying distances from the bed. The water table below the leaching bed was influenced by the hydraulic loading from the leaching bed plus the natural environmental factors such as precipitation and evapotranspiration. The water table fluctuations at a certain distance from the centre of the bed were less influenced by the hydraulic loading. In Figure 3, the significant water table fluctuations are numbered for piezometers 29 and 30 and the following notes with the corresponding numbers explain briefly the fluctuations.

1. The natural water table declined slowly at the beginning of the monitoring program.
2. Hydraulic loading ("feed") of 122,700 L/day to the leaching bed was started and the water table rose rapidly.
3. Liquid was observed bubbling through the topsoil and ponding on the ground surface above the bed. The system was hydraulically overloaded and the loading was terminated.
4. The ground water mound declined after the hydraulic loading to the leaching bed was stopped.

5. A rise in the water table was noted, which was due to the infiltration in the spring thaw period.
6. Effluent was discharged into the bed at the rate of 40,900 L/day. Unfortunately, an electrical malfunction developed in the timer allowing the feed pump to operate continuously. A total of  $1 \times 10^6$  litres of effluent was discharged in a four-day period causing a sharp rise in the water table.
7. This was a short rest period to allow the mound to decline.
8. Hydraulic loading was resumed at a rate of 40,900 L/day.
9. This system was shut down for one week and the water table declined.
10. The loading was continued at 40,900 L/day with an increase in the water table mound.
11. An ice blockage in the line from the pump to the feed tank caused the system to be shut down for one week. The ground water mound declined.
12. Loading was resumed at 40,900 L/day with a corresponding mound.
13. The water table rose sharply due to the spring thaw.
14. This was a period of decline and stabilization of the water table after the spring peak levels had occurred. The loading to the bed was still maintained at 40,900 L/day.
15. This was a continuous loading period of 40,900 L/day from July to December, 1978. The ground water levels remained relatively steady with minor fluctuations due to rainfall and evapotranspiration.
16. The hydraulic loading was stopped and the water table began to decline.
17. This was the spring thaw period, which caused a rise in the water table.

#### ANALYSES OF WATER TABLE MOUNDING

Two methods were used to compute the magnitude of the ground water mound. The first one was proposed by Hantush(1,2) and is a deterministic solution, the second one was due to Sykes(3) and is a finite-element computerized numerical model. First, the selection of the values of the aquifer (or soil) parameters used in the calculations will be briefly discussed. Then, the calculated results will be compared with the field experimental data obtained in the periods when the hydraulic loadings were 122,700 L/day and 40,900 L/day.

In the analyses, the values of the specific yield (s), hydraulic conductivity (k), and the height of the water table above the base of the aquifer (h) are required. These values were determined in the field exploration program. Because of the natural variability of the materials in the aquifer, some judgement was required in the selection of the values of these parameters used in the calculations.

A value of 0.2 was chosen for the specific yield (s). The selection was based on literature data for silt materials(4). In addition, the results of measurements on the bulk porosity and the degree of saturation on soil samples obtained at the test site were used as a reference.

As shown in Figure 2, the material beneath the north part of the leaching bed is sandy silt, which is more permeable than the clayey silt below the south part of the leaching bed. Theoretically, in a nearly horizontal ground water flow from a water table mound at the test site, the more permeable soil (ie the sandy silt) under the leaching bed should exercise more influence on the mounding. Therefore, the k values of sandy silt were used in the calculations of the mounding. The average k value of the sandy silt obtained by the in situ "falling head" method(5) and the in situ "infiltration" method(6) in piezometers was  $3.7 \times 10^{-4}$  cm/s. The average k value measured by the in situ "constant head" method(7) in the "Geonor" piezometers was  $3.5 \times 10^{-5}$  cm/s. This smaller k value could be attributed to the field method and the smaller-sized "Geonor" piezometers which were driven into the soil. The piezometers used in the variable-head methods were installed in augered holes and were much larger than the driven-type piezometers.

As shown in Figure 2, the height of the water table above the bedrock is not constant and increases in the direction towards Ouse river. However, only a constant h value can be used in Hantush's analysis. Based on the results of the field exploration, an average value of 12 m was selected, which was approximately equal to the difference in elevations of the bedrock and the initial water table beneath and adjacent to the leaching bed. In the analysis, another value of 8 m was also used and this value was approximately equal to the average thickness of the sandy silt beneath the initial water table in the vicinity of the leaching bed area.

The calculated results for a number of combinations are summarized in Figures 4(a), (b) and (c) for comparison with the field data. As shown in Figure 4(a), the average data of piezometers 24, 25, 29 and 30 compare well with the theoretical data for the k value of  $3.7 \times 10^{-4}$  cm/s. However, the theoretical mounding for the k value of  $3.5 \times 10^{-5}$  cm/s is greater than that of the actual measurements. With these field data, a "back-calculated" k value of  $5.0 \times 10^{-4}$  cm/s was obtained, which was later used for the computations of the water table mounding at other piezometer locations.

In Figure 4(b), the comparison of the experimental data with the theoretical curves is reasonably good even though the  $k$  values are quite different. The better comparison could be attributed to the short period of the hydraulic loading and the distance of the piezometers from the centre of the bed (ie, smaller mound at larger distance from the centre of the bed). For piezometers 23 and 28, the theoretical and experimental results compare poorly (see Figure 4(c)). This could be due to:

- (i) different soil conditions on the south part and the north part of the leaching bed, and
- (ii) the  $k$  values were for the soil below the north part of the leaching bed (ie, sandy silt).

The magnitude of the water table mounding under the leaching bed at the site was also calculated by Sykes' finite-element computer model. In Figures 5 and 6, the computed results by Sykes' model for two loading rates are compared with those of Hantush for a constant  $h = 12$  m.

Because Sykes' finite-element model has the flexibility of varying the input data (eg,  $k$ ,  $h$ ,  $s$  and hydraulic loading rate) in each element, it was decided not to use a constant  $h$  in the additional analyses. Instead, the thickness of the aquifer was calculated by subtracting the elevation of the water table prior to the testing program from the elevation of the bedrock. In Figures 7 and 8, the computed results are compared with results by the Hantush analyses, in which the value of  $h$  was assumed to be 12 m.

As seen in Figures 5 to 8, good comparison of the results were observed between Sykes' and Hantush's methods.

During week 44 to week 126, with the exception of a few periods of short duration, the hydraulic loading rate was 40,900 L/day. The fluctuations of the water table beneath the leaching bed (see Figure 3) was influenced by two factors: (i) the hydraulic loading from the bed, and (ii) precipitation and evapotranspiration at the site. Because Hantush's method does not take into account the effect of evapotranspiration and precipitation and it also assumes a constant hydraulic loading rate during the loading period, it becomes quite difficult to compare the short-term minor fluctuations of the water table with the theoretical curve. Fortunately, in design, it is the maximum rise of the water table which is of practical significance. Therefore, the comparison of the calculated maximum rise of the water table mound with what was measured in the field would be of prime interest. The theoretical rise of the water table at piezometer 30 was calculated by Hantush's method for several cases and the results are summarized in Figure 9. Referring to the data of piezometer 30 in Figure 3, the water table elevation 26.5 m at week 12 could be considered as the "base line" for the measurement of the net water table mound. Therefore, in April 1978, the maximum increase of the water table was 2.8 m. This

large increase was the result of the combined effect of the hydraulic loading to the leaching bed and the infiltration of surface water from the 1978 spring thaw. From week 105 to week 126, the net rise of the water table at piezometer 30 was maintained at about 1.6 m and there was very little fluctuation in the elevation of the water table. However, for piezometer 2, the elevation of the water table during the same period was approximately at the same elevation before the hydraulic loading of 40,900 L/day was applied to the bed. It should be noted that piezometer 2 was not affected significantly by the hydraulic loading in the bed because it was located far from the leaching bed (see Figure 1). Thus, the fluctuations of the water table at this location were mainly due to precipitation and evapotranspiration. Because piezometers 30 and 2 were located not more than 150 m apart, it may be assumed that the climatic influence on the water table at these locations was about equal. Therefore, if the water table at piezometer 30 had not been affected by the many weeks of hydraulic loading, the water table would have returned close to elevation 26.5 m. However, the net rise of the water level in piezometer 30 with respect to elevation 26.5 m was 1.6 m. Therefore, it can be inferred that this ground water mound was the result of many weeks of hydraulic loading in the leaching bed.

The measured net rise (1.6 m) in the water table was smaller than the predicted values presented in Figure 8. The main reasons could be:

- (i) the long-term average effective hydraulic loading was less than 40,900 L/day, considering the net effect of infiltration and evapotranspiration,
- (ii) the field-determined and the "back-calculated"  $k$  values were too small, and
- (iii) the value of  $h$  was greater than the assumed 12 m.

#### DISCUSSION

From this extensive ground water monitoring study conducted at Norwood, Ontario, experience and knowledge can be gained in two areas:

- (i) the fluctuations of the water table beneath a large leaching bed, including the relatively important influence of precipitation on water table mounding, and
- (ii) the use of two mathematical models, (ie. Hantush and Sykes) for the prediction of water table mounding beneath a recharge area.

Both the Hantush and Sykes methods gave reasonable, although conservative, predictions of the water table mounding under a large leaching bed provided that,



- (i) the "back-calculated"  $k$  value or the proper selection of the field-determined  $k$  value was used, and
- (ii) the rapid ground water rise caused by a large quantity of infiltration at the time of spring thaw was not considered.

These assumptions lead to a number of practical considerations in the prediction of the water table mounding under a recharge basin (or area) such as a leaching bed.

(i) In the calculation of the magnitude of the water table mound, values of aquifer parameters are required. In this study, these values were obtained either by "back-calculation" from the field data or by actual measurements in a number of boreholes made at the site. The mounding prediction was reasonable when the "back-calculated"  $k$  value or the  $k$  value determined by the "falling head" and the "infiltration" methods was used. As a result of this study, it is felt that the "falling head" and the "infiltration"  $k$  tests in piezometers are suitable for sandy silt soils. However, it is not certain whether these field tests would yield reasonable  $k$  results for clayey soils for the water table mounding calculations. Perhaps, a model-scale field test or a field pumping test would give more meaningful  $k$  and specific yield ( $s$ ) results for fine-grained, clayey soil deposits.

(ii) In this study, it was found necessary to consider the water table rise caused by the spring infiltration in order not to underestimate the maximum mounding. As indicated in Figure 3, the rise of the water table at various seasons was different. This was only reasonable because of the stochastic nature of climatic conditions. Therefore, in the design, it would be necessary to study weather data (precipitation, evaporation, etc) at a potential site for as many years as practically feasible. In addition, prior to the construction of a leaching bed at a potential site, it is useful to install a number of piezometers at the site to monitor the natural fluctuations of the water table for a minimum of one year. The one-year water table fluctuation data, together with the historical weather data can be used to make a reasonable estimate of the maximum natural rise of the water table at a potential site. A statistical approach may be used to predict the probability of the occurrence of the maximum rise in the water table due to spring thaw infiltration. In selecting the probable maximum rise of the water table due to spring infiltration and the hydraulic loading, the designer should consider the chance for the occurrence of this maximum and the effect of surface flooding due to the excessive rise of the water table.

As a precautionary measure, a few piezometers should be installed near the centre of the leaching bed and the water table should be monitored during the operation of the bed. It may also be feasible to adjust the hydraulic loading rate in the leaching bed at the time of the spring thaw in order to avoid flooding of the bed.

(iii) In this study, both the Hantush and Sykes methods were used for the calculation of the water table mound. Because of the simplicity of the Hantush method, it would be a more practical tool for routine calculations. Furthermore, at the present time, the inaccuracy in the prediction of mounding lies more in the inability to practically assess the overall aquifer characteristics than in the predictive method being used.

However, it should be pointed out that the Sykes model has a number of flexible features which Hantush's method does not have. For example, in each element of Sykes' model, the soil properties, the infiltration rate and the thickness of the aquifer can be different. Therefore, Sykes' model can be used as a refined design tool if the soil properties at a potential site can be measured with reasonable accuracy. In addition, the Sykes' finite-element model can more accurately represent the ground water loading caused by seasonally varying infiltrations. It is suggested that for sites in which natural infiltration or soil heterogeneities are important, a finite-element type analysis may be warranted.

#### CONCLUSIONS

1. Many factors affected the fluctuations of the water table beneath a large leaching bed including precipitation, evapotranspiration, and the hydraulic loading rate. The relative significance of these factors on the movement of the water table depends on the site and on the seasons.
2. Two mathematical models (Hantush's and Sykes') were used to predict the magnitude of the water table mounding. For identical values of input parameters similar results were given by the two models. Because of the relative simplicity in the use of the Hantush method, it is more suitable as a routine design tool. However, the flexibility of Sykes' finite-element model should not be overlooked, and the numerical method may be used for more complicated site conditions if the aquifer characteristics can be measured with greater accuracy.
3. In using Hantush's solution, it is recommended that the "falling head" and the "infiltration" tests be used to measure the hydraulic conductivity (k) values of sandy silt soils. In addition to the measurements of k and specific yield (s) at individual locations, a detailed study of the soil stratigraphy at the proposed site should be carried out so that a proper interpretation of the aquifer data can be made.
4. The Hantush method can be used to predict the mounding due to a constant hydraulic loading but it cannot be used to predict the mounding caused by the spring thaw infiltration. From this study, it is recommended that an estimate

of the rise in water table due to the infiltration of surface water be made on a statistical basis according to the weather data and a minimum of one year's observational data on the natural fluctuations of the water table. The magnitude of the maximum water table rise should be equal to the sum of the maximum rise caused by the hydraulic loading and that due to surface infiltration.

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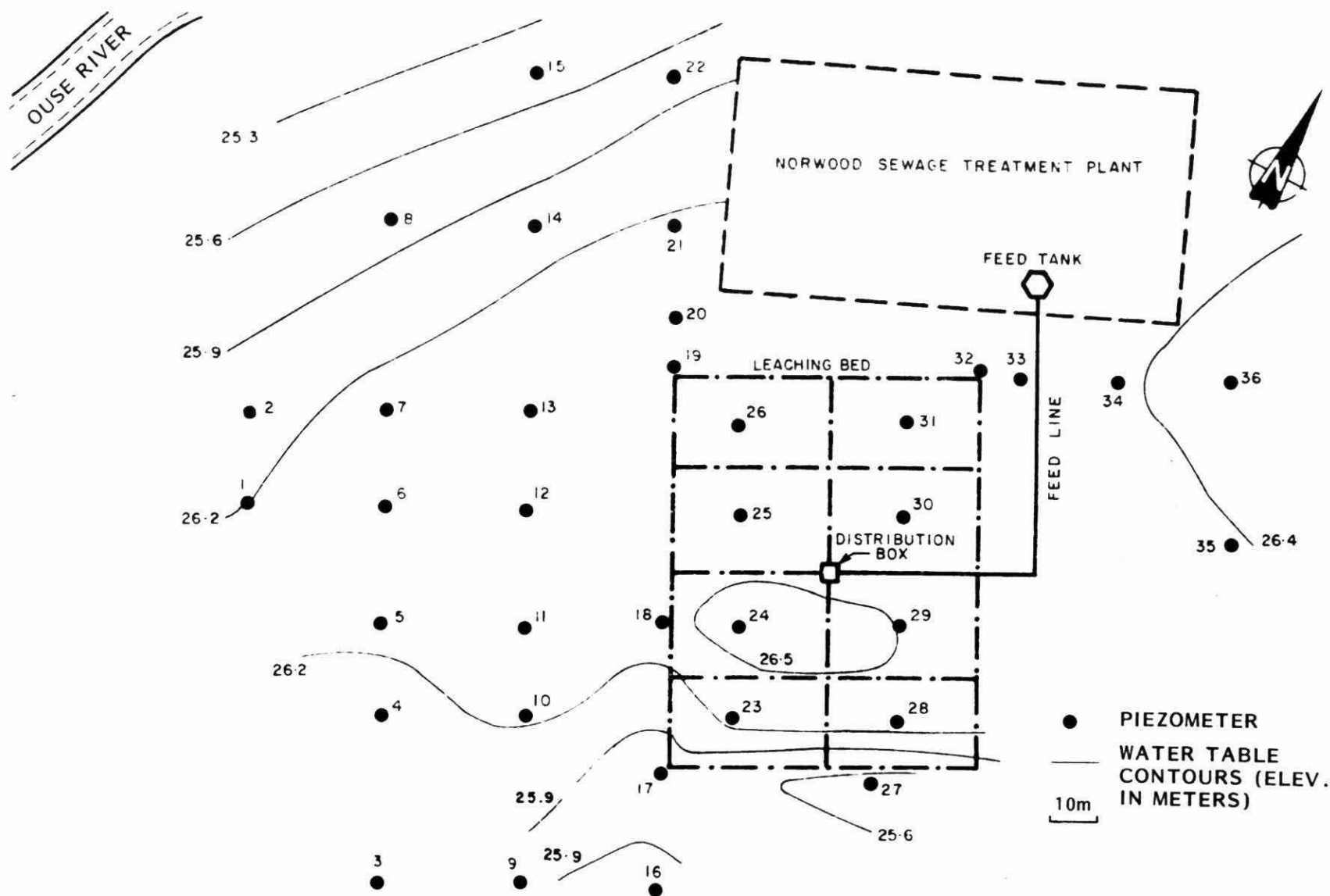


FIGURE 1  
LOCATION OF PIEZOMETERS AND INITIAL WATER TABLE CONTOUR LINES

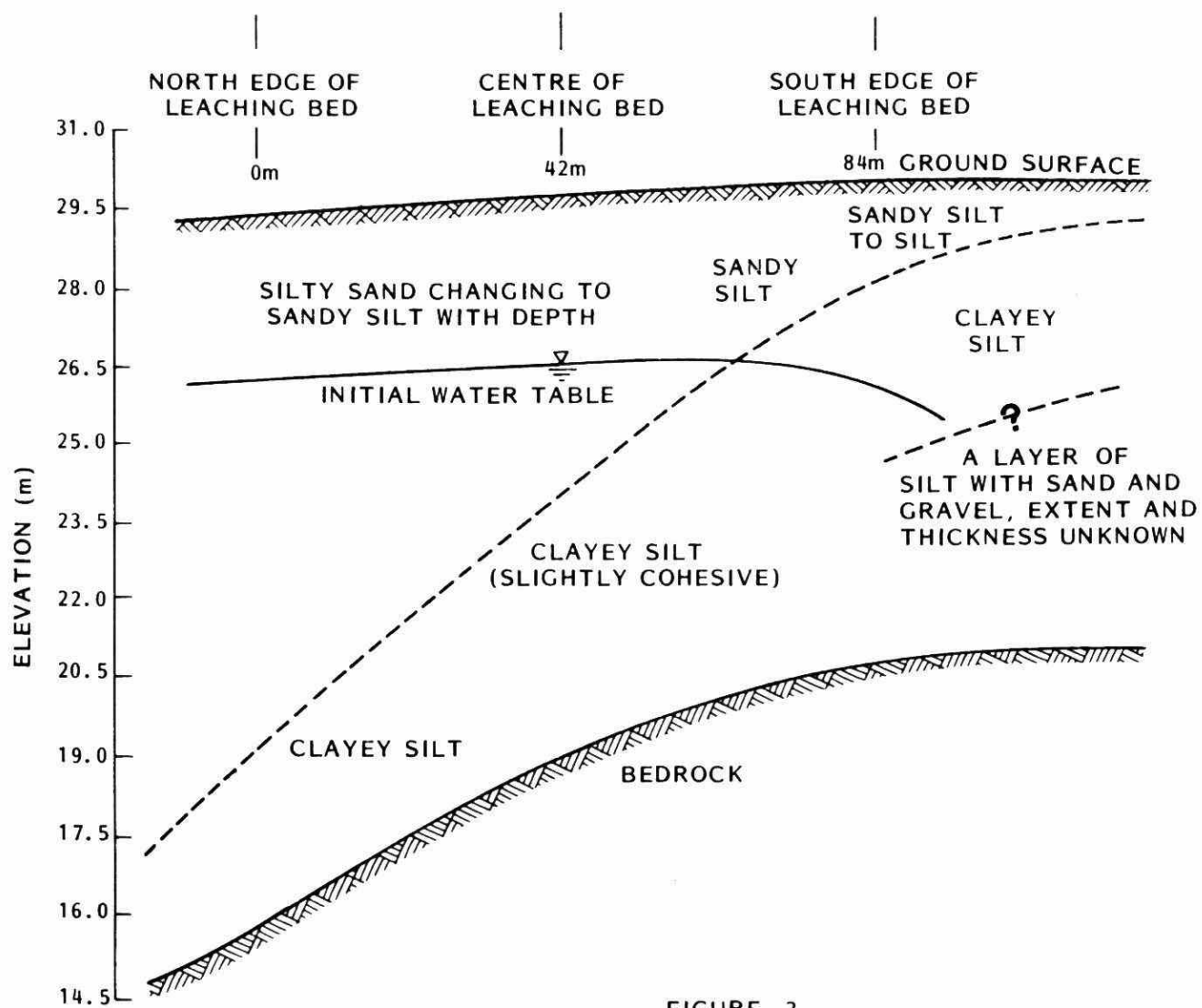


FIGURE 2  
SOIL STRATIGRAPHY THROUGH THE N-S CENTRE-LINE OF THE LEACHING BED

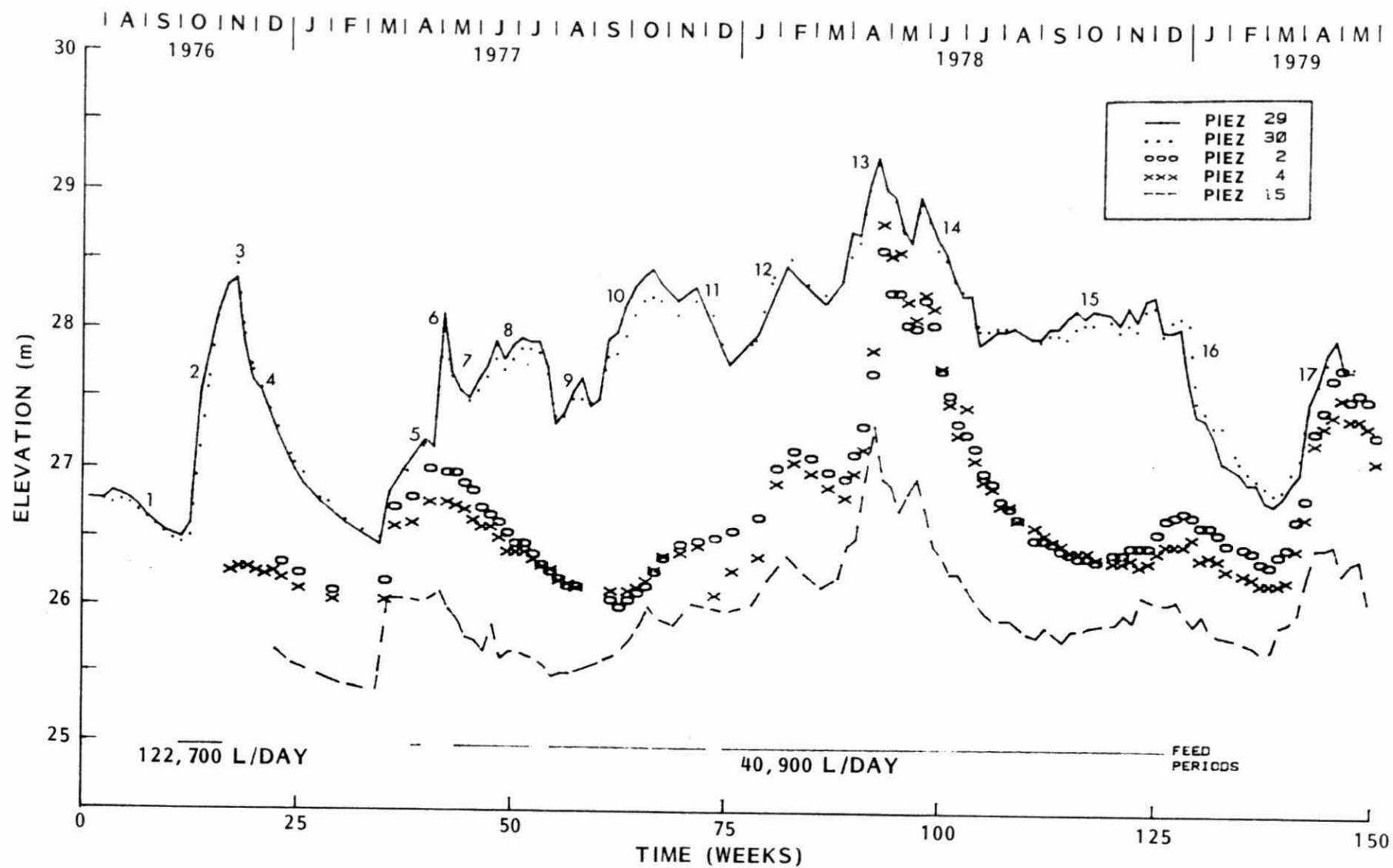


FIGURE 3  
COMPARISON OF GROUNDWATER FLUCTUATIONS WITHIN AND ADJACENT TO THE LEACHING BED

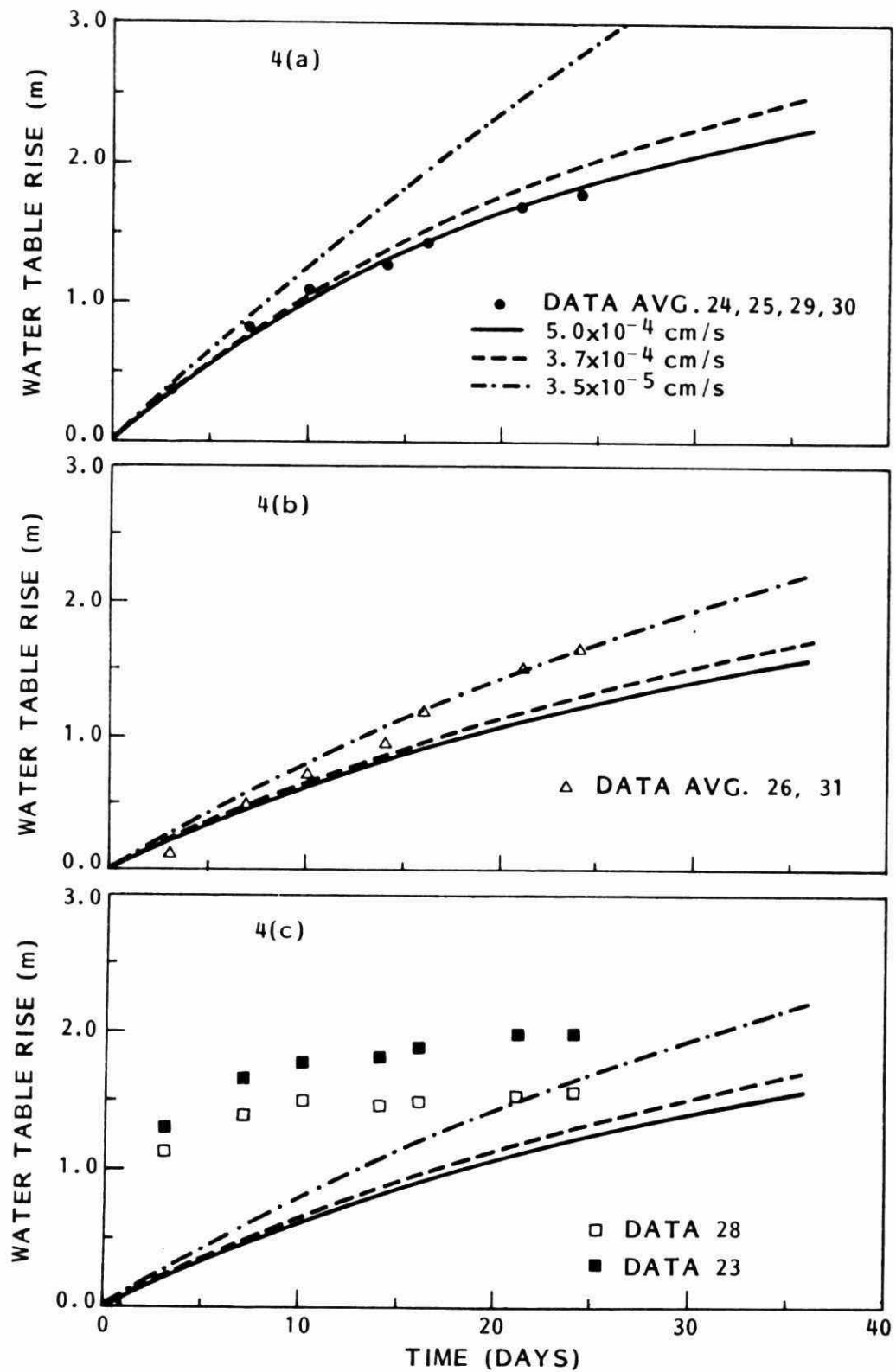


FIGURE 4  
COMPARISON OF THEORETICAL AND EXPERIMENTAL GROUNDWATER  
MOUNDING DATA (LOADING RATE 122700 L/DAY,  $h=12\text{m}$ ,  $s=0.2$ )

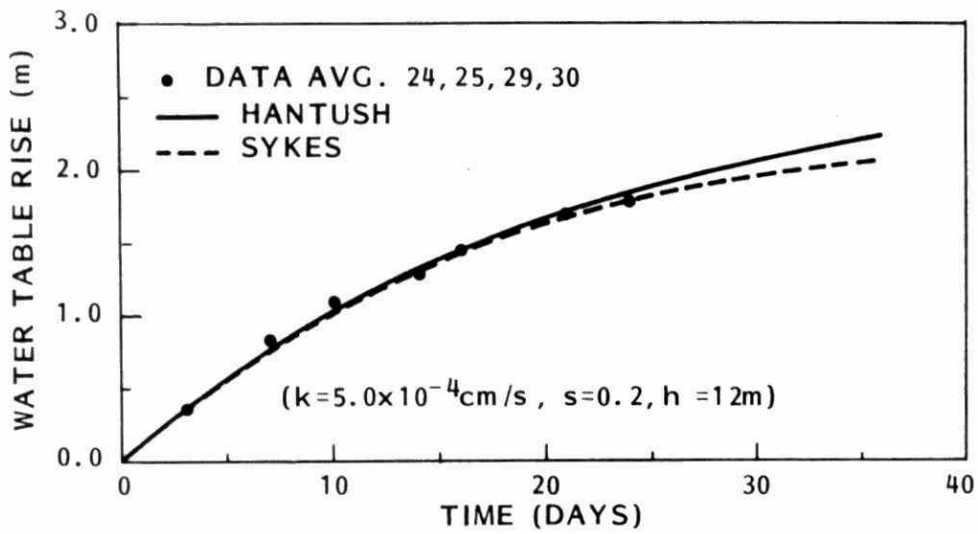


FIGURE 5  
SYKES' COMPUTED RESULTS COMPARED TO HANTUSH  
(LOADING RATE 122700 L/DAY)

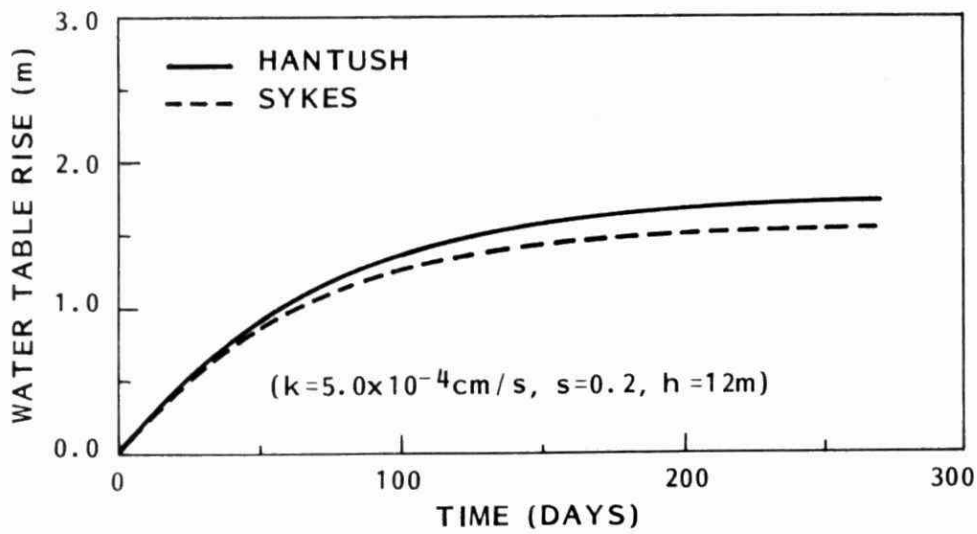


FIGURE 6  
SYKES' COMPUTED RESULTS COMPARED TO HANTUSH  
(LOADING RATE 40900 L/DAY,  
PIEZOMETER LOCATION 30)

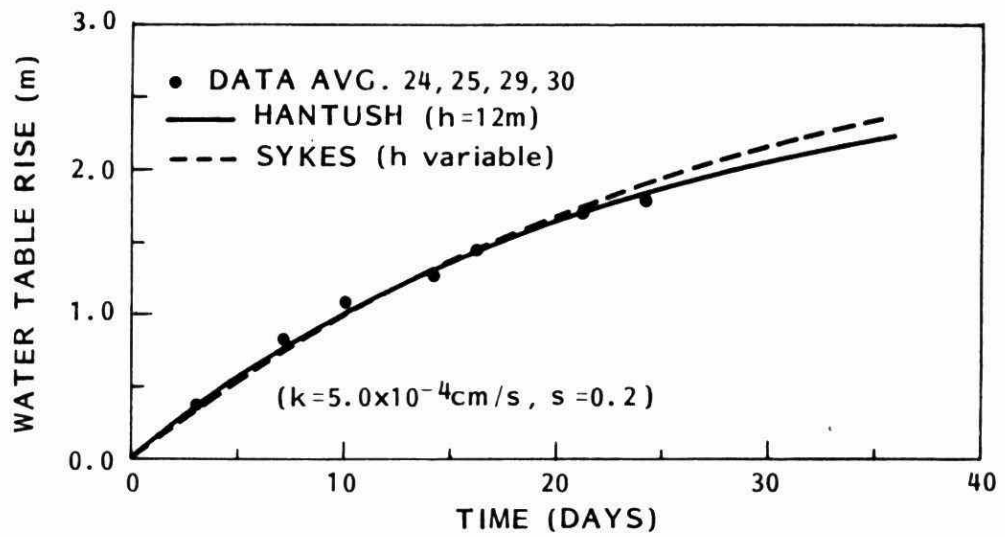


FIGURE 7  
SYKES' COMPUTED RESULTS COMPARED TO  
HANTUSH (LOADING RATE 122700 L/DAY)

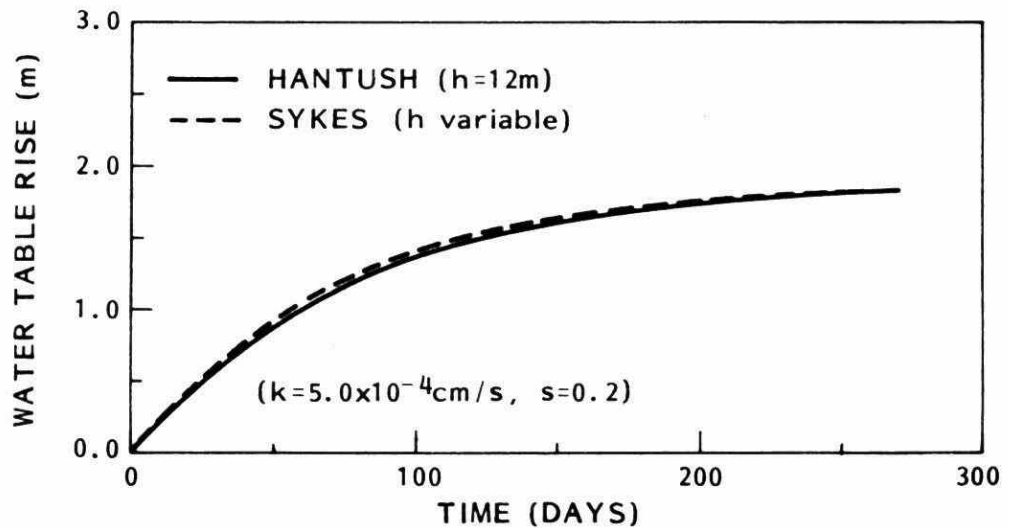


FIGURE 8  
SYKES' COMPUTED RESULTS COMPARED TO  
HANTUSH (LOADING RATE 40900 L/DAY,  
PIEZOMETER LOCATION 30)

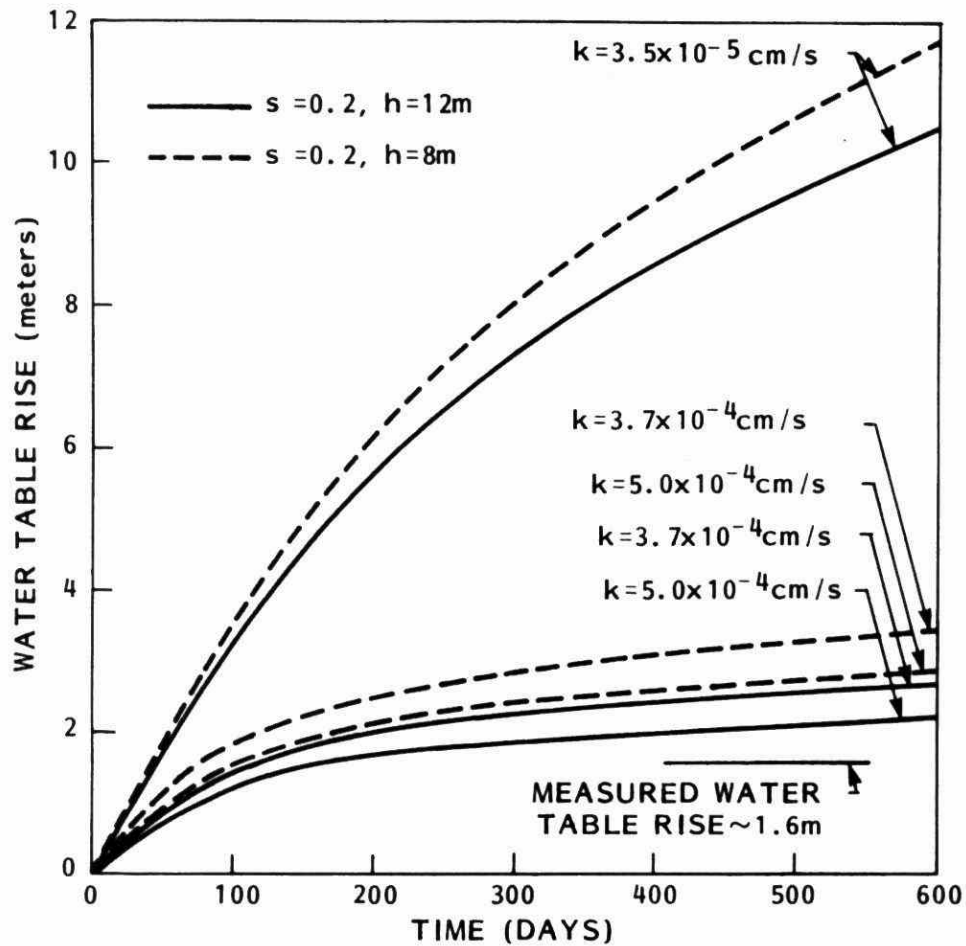


FIGURE 9

COMPARISON OF HANTUSH CALCULATED WATER  
TABLE RISE WITH FIELD DATA AT PIEZOMETER 30  
(LOADING RATE = 40,900 L/day)



ARSENIC WASTE TREATABILITY STUDIES - DELORO

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ABSTRACT

Treatability of leachate and runoff containing high levels of dissolved arsenic was studied at the bench and pilot scales. The objective of the study was to develop design parameters for full-scale treatment facilities which would be used to reduce arsenic concentrations in treated effluents to below 5.0 mg/L.

Studies included the evaluation of the effect of chemical dosages, contact times, sequence of chemical additions and temperature on arsenic removals for the ferric chloride-lime treatment process. Solids separation with the aid of a polymer, and sludge stabilization were also appraised.

Based on the results obtained, the two stage chemical addition process at a Fe/As molar ratio of 2/1 is recommended. Lime dosage should be such to attain a final effluent pH within a range of 9.0 to 11.0. On the average this is achieved with a lime/As ratio of 3/1. Secondary flocculation with a polymer at a polymer/As ratio of 1/45 was also required to enhance floc settling rates and solids separation.

## BACKGROUND

The study was undertaken to develop design data for a fullscale arsenic removal plant for an abandoned mining and smelting site. At one time the site belonged to the former Deloro Mining and Smelting Company Limited, located 45 km north of Belleville, Ontario. Past activities on the site included gold mining and refining of silver, cobalt and uranium ores. A major byproduct from these operations was arsenic trioxide. Until 1958, the recovered arsenic was sold and used in the manufacturing of arsenic based pesticides. When this market declined, recovered arsenic was indiscriminately stockpiled on site. Consequently, surface runoff and leachates containing high levels of arsenic contributed to arsenic contamination of the Moira River which flows through the plant site. Since 1958, both the OWRC and MOE maintained a regular surveillance program on and around the Deloro property. In 1961 the plant was permanently closed.

In 1966, an onsite arsenic treatment plant was approved and built. The control of arsenic was, however, inadequate due both to poor treatment and to a totally inadequate runoff/leachate collection system.

In 1979, following bankruptcy of the owners, the Ministry of the Environment (MOE) assumed management of the site. Since this time, the Southeastern Region of the MOE in cooperation with a consulting firm, have proposed plans and recommendations to reduce arsenic contamination in the Moira River.

A major recommendation by the consultant was to build a new treatment plant capable of consistently achieving residual arsenic concentrations not exceeding 5 mg/L.

The present study was developed in order to facilitate the design of a new arsenic treatment plant through bench and pilot scale studies.

## OBJECTIVES AND SCOPE

The major objective of this study was to provide design data for a fullscale arsenic waste treatment plant using the ferric-lime process. Treatment objectives called for an effluent arsenic concentration not exceeding 5.0 mg/L.

The design data were first developed at the bench scale level (jar tests and settling column tests) and were then further evaluated by onsite pilot plant operations.

During the study the following design requirements were evaluated:

1. Optimization of ferric chloride and lime dosages.
2. Selection and optimization of polymers to enhance settling of primary floc.
3. An evaluation of the effects of temperature, chemical mixing rates and contact times on arsenic reduction.
4. An evaluation of settling characteristics of primary and secondary flocs.
5. A preliminary assessment of sludge stability.

## EXPERIMENTAL PROCEDURES

### Onsite Sample Collection - Bench-Scale Studies

Grab samples of untreated arsenic waste were collected during different seasons of the year to cover the wide range of prevailing arsenic concentrations. The samples, consisting of about 100 L each, were brought to the MOE Toronto Laboratories for analysis and treatment studies. A detailed description of the site, including existing leachate/runoff collection and treatment facilities, is given elsewhere (1).

- (1) Reid, Crowther and Partners Limited, Toronto, Ontario, "A Remedial Clean-up Program For The Deloro Site", June, 1980.

## TREATMENT EVALUATION

### Jar Test Studies

A 6 unit Phipps and Bird variable speed stirrer was used for jar tests. Sample volume for each test was one litre. Chemicals used for jar testing were ferric chloride ( $\text{FeCl}_3$ ), lime [ $\text{Ca}(\text{OH})_2$ ], and a selection of polyelectrolytes (polymers). Jar testing was done with and without the use of a polymer. For ease of dosing,  $\text{FeCl}_3$  was prepared as a 5.0% W/V  $\text{Fe}^{+3}$  solution and lime as a 5.0% W/V  $\text{Ca}(\text{OH})_2$  slurry. Polymers were initially prepared as 0.5% W/V stock solutions which were then diluted to 0.1% just prior to use.  $\text{Fe}^{+3}$  was usually dosed in increments of 50 mg/L to attain nominal Fe/As molar ratios in the range from 1/1 to 4/1. Lime was dosed to attain a pre-selected final pH.

### Settling Column Studies

The purpose of these studies was:

1. Evaluation of arsenic removal at a larger scale using optimized jar test conditions.
2. Establish settling rates of the chemical floc.
3. Production of sufficient sludge quantities for sludge characterization.

The settling column tests were done in a 150 mm diameter by 1500 mm high translucent column having sampling ports at 300 mm intervals. A schematic of the equipment used for this test is shown in Figure 1. Chemical dosages evaluated for primary flocculation covered nominal  $\text{Fe}^{+3}$ /As ratios from 1/1 to 4/1.

### Sludge Dewatering and Stability

Upon completion of the settling tests, the supernatant above the settled sludge was drained and/or syphoned off. The remaining chemical sludge was removed from the settling column and allowed to thicken in large beakers with subsequent decantation of the clear supernatant. This sludge was further dewatered by batch centrifugation at 10,000 rpm for 10 minutes (including acceleration and deceleration times). The resulting sludge cake was air dried and analyzed for total solids and arsenic. Analysis for sludge characteristics and sludge stability were done at the

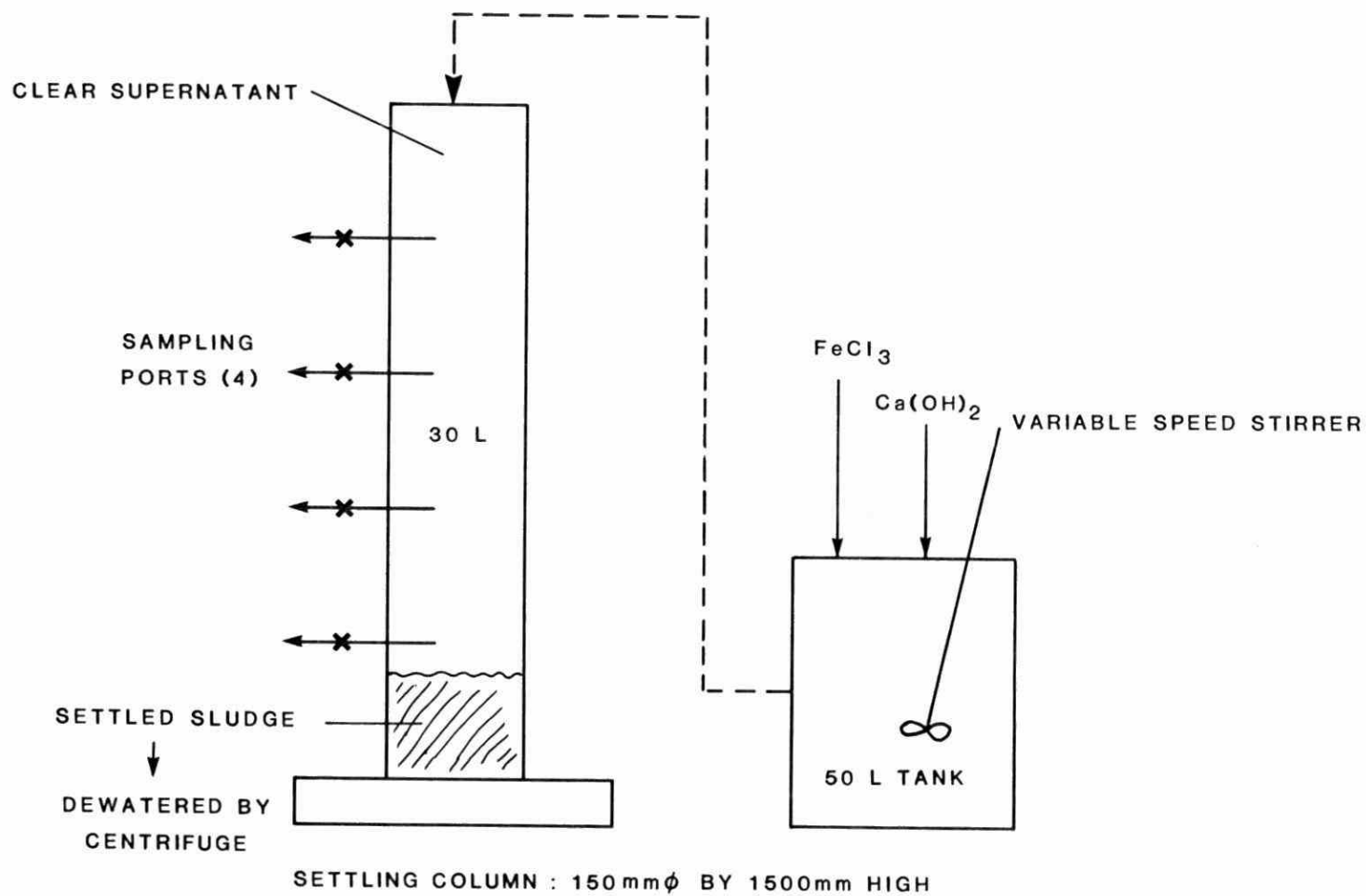


FIGURE 1 SCHEMATIC OF EQUIPMENT FOR SETTLING COLUMN TEST.

MOE Main Laboratory and are based on air dried sludge.

Arsenic release (sludge stability) from these sludges was determined by MOE standardized leachability tests using both  $\text{NH}_4\text{Cl}$  solution at pH 5.5 and distilled water. Samples of wet sludge cake containing the equivalent of 2.5 g of air dried solids were leached in parallel with 50-60 ml of the above mentioned solutions. Leachate was collected for the duration of the 16 hour test period.

#### Onsite Pilot Plant Operation

A pilot-scale arsenic treatment plant was set up and operated at the Deloro site by staff of the Southeastern Region, MOE. The pilot plant is schematically shown in Figure 2. Overall equipment dimensions and nominal operating volumes are also given in Figure 2. The system was designed for hydraulic flow-rates in the range from 10 to 30 L/min. Major equipment included an influent feed pump, ferric, lime and polymer mixing tanks, a final clarifier and associated chemical storage tanks and chemical dosage pumps.

Table 1 summarizes the operating and test parameters for the study program. Principal operating conditions included sequence of chemical addition,  $\text{Fe}^{+3}/\text{As}$  molar ratio, mixing times for ferric, lime and polymer, final effluent pH, sludge recycle, and clarifier overflow rates.

The pilot-scale process was operated on a daily basis, i.e. it was started-up in the morning, shut-down, drained and cleaned-up in the evening. A period of 2-3 hours was allowed in the morning for the process to achieve steady-state operation. Grab samples were taken over the next 5-6 hours for arsenic analysis. The process was carefully monitored and adjusted during the entire period. Each process was evaluated for about two weeks duration. The conventional two-stage chemical addition process with an Fe/As ratio of 2/1 was evaluated for an additional week. Further information on the processes studied and equipment used, can be obtained by contacting MOE staff of the Southeastern Region (2).

(2) Ramshaw, C., "Pilot Plant Operation at Deloro", Summer 1981, MOE, Southeastern Region, Unpublished Results.

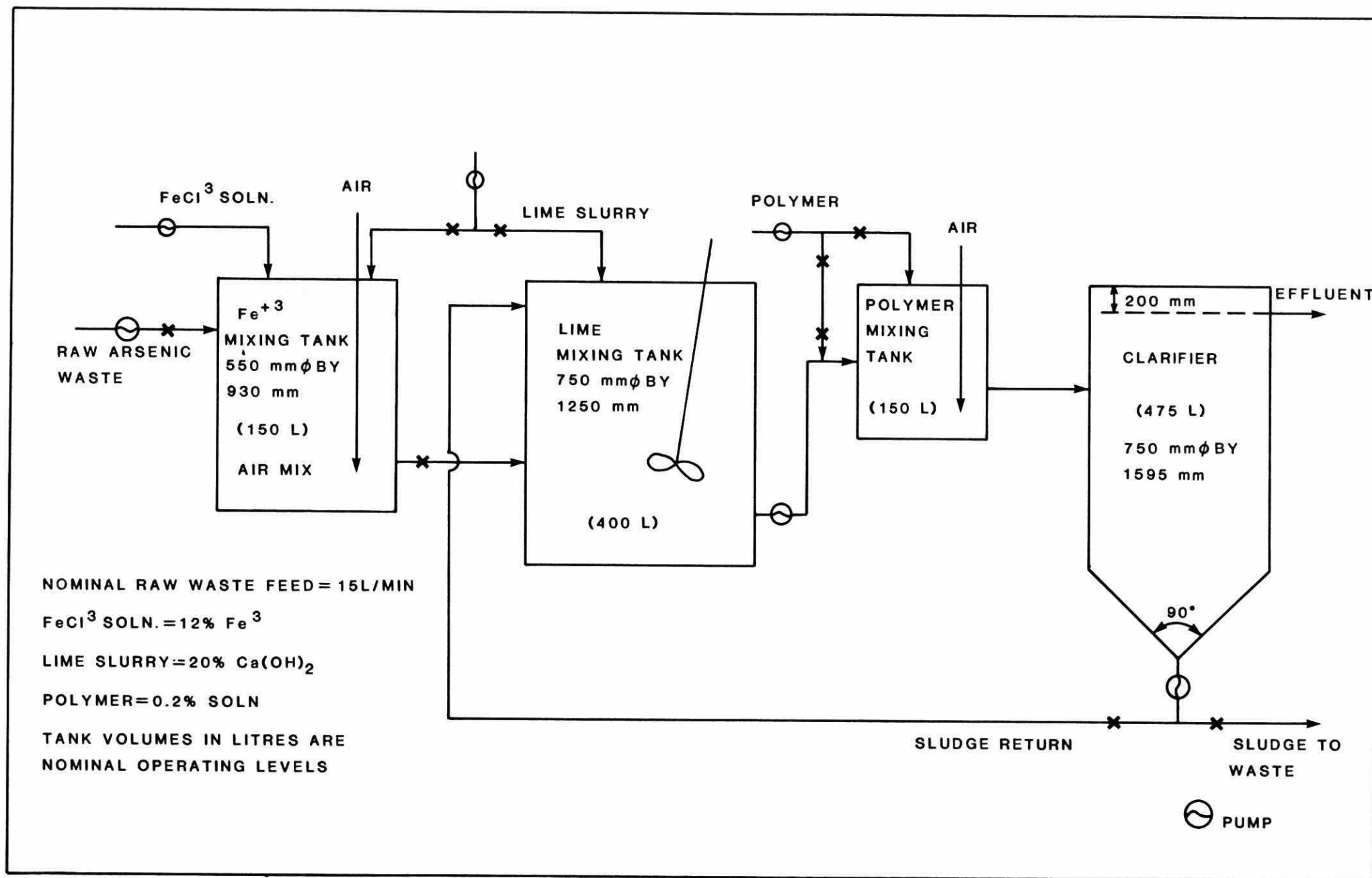


FIGURE 2 SCHEMATIC OF THE BASIC FERRIC-LIME PROCESS ARSENIC PILOT TREATMENT PLANT AT DELORO.

TABLE 1

## SUMMARY OF PROCESS AND TESTING PARAMETERS - PILOT PLANT

PROCESS PARAMETERS

	<u>Conventional 2 Stage*</u>	<u>Conventional 1 Stage*</u>	<u>High Density 2 Stage*</u>
Fe <sup>+3</sup> /As Ratio	1/1-2/1	1/1-2/1	1/1-2/1
Feed Rate L/min	10-30	10-30	10-30
Final pH (Lime)	9.0-11.5	9.0-11.5	9.0-11.5
Polymer	with/without	with/without	with/without
Retention Time - Fe <sup>+3</sup> Tank	Yes	-	Yes
Retention Time - Lime Tank	Yes	-	Yes
Retention Time - Fe <sup>+3</sup> Lime Tank	-	Yes	-
Retention Time - Polymer	Yes	Yes	Yes
Clarifier Overflow Rate	Yes	Yes	Yes
Sludge Return	-	-	Flowrate

TEST PARAMETERS

Raw Waste	As, pH, Flowrate	As, pH, Flowrate	As, pH, Flowrate
Fe <sup>+3</sup> Treated Waste	pH	-	pH
Fe <sup>+3</sup> Lime Treated Waste	pH, TSS, Settleability	pH, TSS, Settleability	pH, TSS, Settleability
Clarifier Overflow	As, pH, SS, Flowrate	As, pH, SS, Flowrate	As, pH, SS, Flowrate
Clarifier Underflow	TSS, Flowrate, Filterability	TSS, Flowrate, Filterability	TSS, Flowrate, Filterability

\* See Appendix for explanation of process definitions.



## RESULTS AND DISCUSSIONS

### Raw Arsenic Waste Characteristics

Arsenic concentrations in samples collected during the study period varied from 170 to 750 mg/L. Typically, the higher arsenic concentrations corresponded to periods of wet weather including snowmelt. Analysis showed that, essentially all of the arsenic was present in soluble form.

### Jar Test Studies

#### Effect of Mixing Time on Arsenic Removal

The effect of sequential mixing times following the addition of ferric chloride and lime are illustrated in Table 2. The results indicate that, for a given Fe/As ratio and pH, arsenic removal was not significantly affected for the range of mixing times studied. The variable arsenic removals at Fe/As ratio of 0.8/1 reflect unstable process conditions when treatment was done with an inadequate Fe/As ratio and were not due to changes in mixing time. It must, however, be pointed out that sufficient mixing to disperse the chemical quickly and evenly into the wastewater is absolutely essential to the successful operation of the process. It was also noted during the study, that as long as adequate initial mixing was provided, rate of agitation (30 to 100 rpm of jar test paddle) during or following ferric chloride and lime additions, had no effect on arsenic reductions.

TABLE 2

## EFFECT OF MIXING TIME ON ARSENIC REMOVAL - JAR TESTS

As-mg/L Raw Waste	Fe/As Ratio	Ca(OH) <sub>2</sub> mg/L	pH Final	Mixing Times-min. Iron	Lime	Residual As mg/L	% As Reduction
530	0.8/1	1000	10.3	1	1	25	95.3
530	0.8/1	1000	10.1	1	2	38	92.8
530	0.8/1	1000	10.5	4	4	13	97.5
530	0.8/1	1000	10.3	5	5	25	95.3
530	1/1	1100	10.0	1	1	6	98.9
530	1/1	1100	10.1	1	2	9	98.3
530	1/1	1075	10.2	4	4	3	99.4
530	1/1	1100	10.2	5	5	5	99.1
400	1/1	750	9.0	5	5	5	98.8
400	1/1	750	9.2	15	15	6	98.5
400	1/1	625	9.2	17	17	4	99.0

#### Effect of Sequence of Chemical Addition on Arsenic Removal

The importance of chemical addition sequence on arsenic removal is clearly illustrated in Table 3. Under identical ferric chloride and lime dosages ( $\text{Fe/As}=0.85/1$ ,  $\text{Ca(OH)}_2=750 \text{ mg/L}$ ), arsenic removal was far superior when lime was introduced after the addition of ferric chloride. In contrast, arsenic removal was the worst when the order of chemical addition was reversed. Simultaneous chemical addition also showed reduced arsenic removal. Although, identical amounts of lime were used for each test condition, the final pH was substantially different for each case. A comparison of the last two results shows that in this case sequence of chemical addition and not final pH affected the arsenic removal process.

#### Effect of Fe/As Ratio or Ferric Chloride Dosage on Arsenic Removal - Jar Tests

Figure 3 shows the effect of varying the Fe/As ratio on percent arsenic reduction and corresponding residual arsenic concentrations. The data in Figure 3 represent test runs from four different samples with overall Fe/As ratios varying from 0.17/1 to 4.2/1. Final pH was maintained between 9.2 and 10.8. To protect the water quality of the Moira River a final pH range of 9.0 to 11.0 was desired. Initial arsenic concentrations and raw waste temperatures are also given in the Figure. Temperature was thought to have some effect on the arsenic removal process. Clearly, the treatment objective of residual arsenic  $\leq 5.0 \text{ mg/L}$  was obtained at Fe/As ratio of 1/1. Further increases in Fe/As ratio up to 4/1 did not produce marked improvements in arsenic removal. In most cases, depending on the raw arsenic concentration, a 99% arsenic reduction was required to attain the treatment objective.

Variations in temperature from  $19^\circ\text{C}$  to  $3^\circ\text{C}$  had no significant effect on arsenic removal for the range of Fe/As ratios studied.

The jar test studies also provided a relative indication of expected settled sludge volumes for different Fe/As ratios. This effect is illustrated in Figure 4 for three different samples. It is clearly seen that sludge volume increased as Fe/As ratio increased.

TABLE 3

EFFECT OF SEQUENCE OF CHEMICAL ADDITION ON FINAL pH AND ARSENIC REDUCTION

Raw As = 400 mg/L, Fe/As = 0.85/l,  $\text{Ca(OH)}_2$  = 750 mg/L

Iron	Lime	pH Final	Mixing Times-min.		Residual As mg/L	% As Reduction
			Iron	Lime		
First	Second	10.0	5	5	17	96
Second	First	9.5	5	5	140	65
Together		8.0		5	55	86

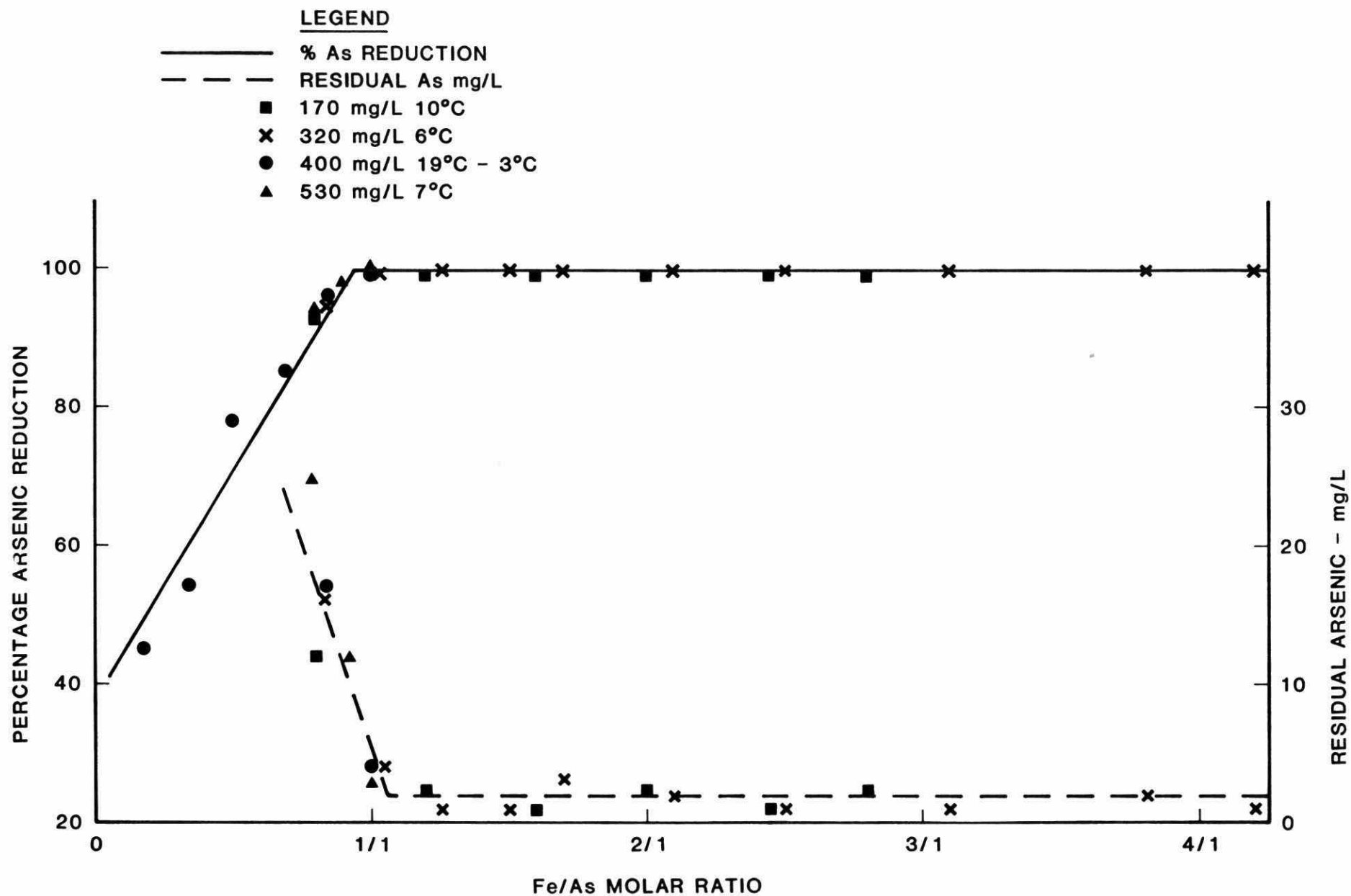


FIGURE 3 EFFECT OF Fe/As RATIO ON ARSENIC REDUCTION

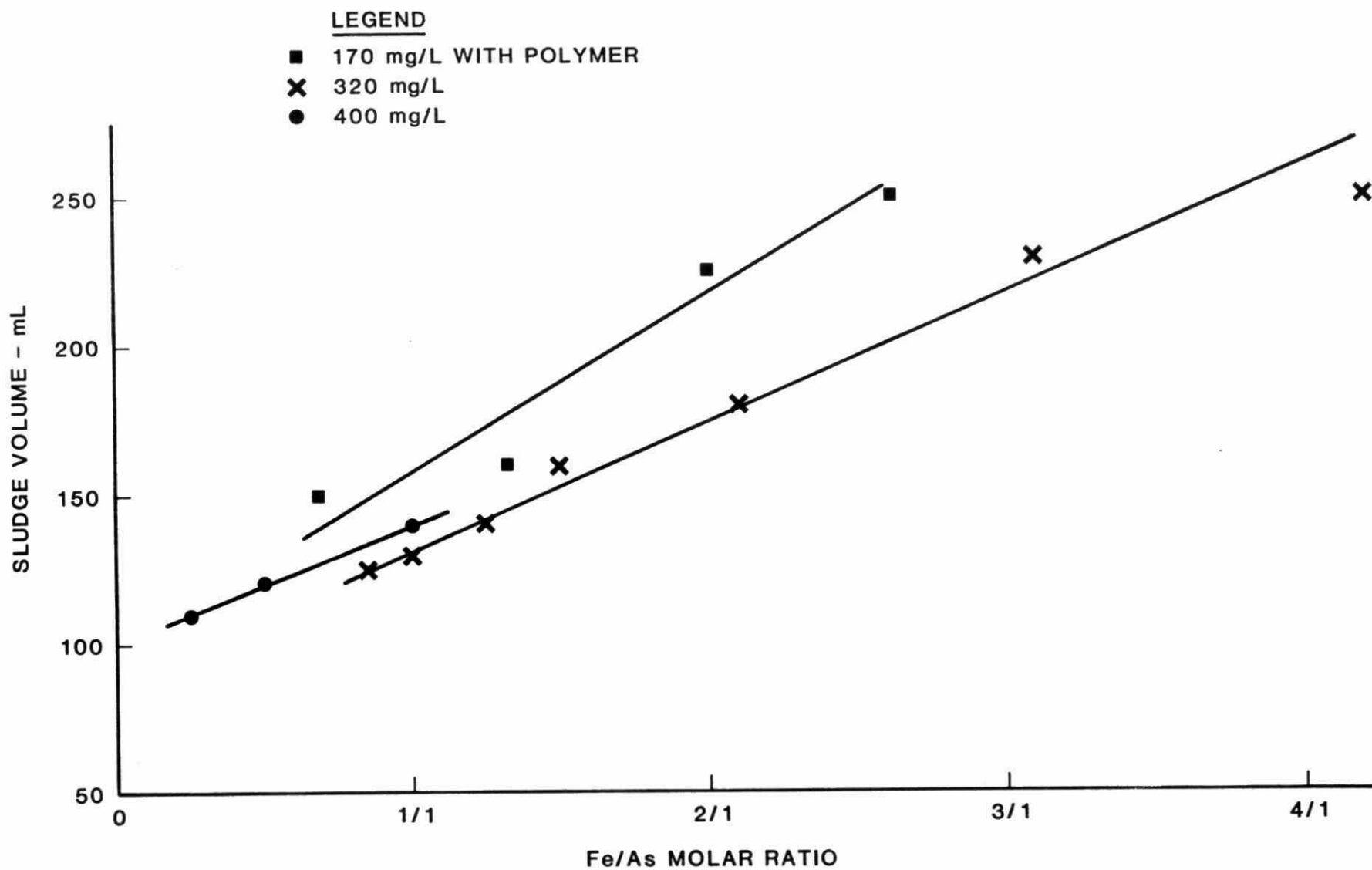


FIGURE 4 EFFECT OF Fe/As RATIO ON SLUDGE VOLUME

#### Effect of Lime Dosage on Arsenic Removals

Table 4 illustrates that arsenic removal can be enhanced by increasing the lime dosage. This only occurred when marginal Fe/As ratios were used which tend to produce unstable arsenic removals. Under these conditions iron deficiency is supplemented by lime which by itself is also an arsenic precipitant.

#### Polymer Selection and Dosage Optimization - Jar Tests

The requirement of a polymer to speed up the settling rate of the chemical floc was recognized early in the study. Basically, the settling rate varied according to the relative floc density which is a function of the raw arsenic concentration, the selected Fe/As ratio and final pH.

Polymer selection was done with a single Fe/As ratio of 2/1 and a final pH of 10. Visual observations such as relative floc formation, floc size, and settling rate were used as guidelines to select suitable polymers. Percol 725 and Percol 730 produced the best results from the available selection of polymers. Both polymers are anionic.

Percol 725 was further evaluated at Fe/As ratios of 0.67/1 to 2.67/1 with a batch of arsenic waste with an initial concentration of 170 mg/L. Polymer dosages and visual observations from these tests are summarized in Table 5. Minimum polymer dosages for adequate settling were 2.0 mg/L and 4.0 mg/L for Fe/As ratios of 0.67/1 to 1.33/1 and 2.0/1 to 2.67/1, respectively. Polymer dosages above these values did not show additional improvements or detrimental effects towards the flocculation or settling process. Furthermore, arsenic removal was not substantially enhanced by polymer addition. The use of a polymer, however, reduced sludge volume.

#### Settling Column Tests

Arsenic removals and associated operating conditions for the settling column tests are shown in Table 6.

TABLE 4

EFFECT OF FINAL pH ON ARSENIC REMOVAL - JAR TESTS

As-mg/L Raw Waste	Fe/As	Lime Dosage mg/L	pH Final	Residual As mg/L	% As Reduction
320	0.84/1	700	10.3	16	95.0
320	0.84/1	750	11.5	<1	>99.7
400	0.85/1	650	9.0	28	93.0
400	0.85/1	700	9.4	21	94.8
400	0.85/1	725	10.0	17	95.8
400	0.85/1	750	10.5	10	97.5



TABLE 5

EFFECT OF POLYMER ON FLOC DENSITY

(Initial Arsenic Conc. = 170 mg/L)

$\text{Fe}^{+3}/\text{As}$	Polymer Dosage - mg/L					
	0	0.5	1.0	2.0	4.0	6.0
0.67/1						
Floc Size	-	med.	med.	Large	Very Large	Very Large
Settling time-sec.	-	120	75	45	30	30
Sludge volume-mL	200	150	125	150	150	150
As-mg/L	16	11	12	12	12	12
1.33/1						
Floc Size	-	med.	med.	Large	Very Large	Very Large
Settling time-sec.	-	120	75	45	30	30
Sludge volume-mL	250	175	160	160	175	175
As-mg/L	3.1	1.4	1.5	1.5	1.6	1.1
2.0/1	-	fine	med.	med.	Large	Very Large
Floc Size	-	-	90	75	30	30
Settling time-sec.	-	-	90	75	30	30
Sludge volume-mL	450	260	250	225	225	225
As-mg/L	1.8	1.0	0.88	1.2	1.0	0.76
2.67/1						
Floc Size	-	fine	med.	med.	Large	Large
Settling time-sec.	-	-	-	-	30	30
Sludge volume-mL	550	350	260	260	250	260
As-mg/L	1.8	1.7	1.5	0.88	1.5	0.94

Polymer evaluated was Percol 725

Floc Size - based on visual observations

Settling time - time floc can be visually observed while settling

Sludge volume - sludge volume measured after 15 minutes of settling

As-mg/L - is As concentration in decanted supernatant (not filtered)

TABLE 6

SUMMARY OF SETTLING COLUMN TESTS WITH  $\text{Fe}^{+3}$  AND LIME

<u>Sample of:</u>		<u>April 16/80</u>	<u>September 4/80</u>		<u>November 6/80</u>			
Raw As concentration	mg/L	530	170	170	320	320	320	320
$\text{Fe}^{+3}$ /As Ratio	-	0.9/1	1.2/1	4/1	1/1	2/1	3/1	4/1
Final pH	-	10.3	10.6	10.5	10.3	10.9	10.8	10.8
Residual Arsenic	-	24	1.0	<1.0	6	4	2	<1
Arsenic Reduction	%	95	99.4	>99.5	98.0	98.8	99.4	>99.7

Samples not filtered for residual As analysis

Mixing Time for Fe - 2 min. and for Lime 5 min.

The range of  $\text{Fe}^{+3}/\text{As}$  ratios varied from 0.9/1 to 4/1. Although a  $\text{Fe}^{+3}/\text{As}$  ratio of 1/1 gave adequate arsenic reduction, the higher  $\text{Fe}^{+3}/\text{As}$  ratios were included to get an indication of the effect of the  $\text{Fe}^{+3}/\text{As}$  ratio on sludge stability.

The sample of April 16, 1980 was treated with sufficient iron to produce a  $\text{Fe}^{+3}/\text{As}$  ratio of 0.9/1. The resulting arsenic removal efficiency of 95% and 24 mg/L residual arsenic indicates that this ratio was inadequate to achieve the desired effluent quality.

The sample of September 4, 1980 was adequately dosed with  $\text{Fe}^{+3}$  at a  $\text{Fe}^{+3}/\text{As}$  ratio of 1.2/1 resulting in a residual arsenic concentration of 1.0 mg/L or 99.4% arsenic removal. In this case, no additional arsenic removal was obtained by increasing the  $\text{Fe}^{+3}/\text{As}$  ratio to 4/1. The latter is likely due to the very low initial arsenic concentrations.

The sample of November 6, 1980 was tested under four different  $\text{Fe}^{+3}/\text{As}$  ratios namely 1/1, 2/1, 3/1 and 4/1. Again, a  $\text{Fe}^{+3}/\text{As}$  of 1/1 provided adequate arsenic reduction of 98% or a residual of 6.0 mg/L arsenic. In this case, it is clearly seen that still lower residual arsenic concentrations can be obtained down to <1.0 mg/L, by increasing the  $\text{Fe}^{+3}/\text{As}$  ratio to 4/1.

For the range of raw arsenic concentrations studied, it was noted that the initial arsenic concentration had some effect on residual arsenic concentration at a fixed  $\text{Fe}/\text{As}$  ratio. Consequently, an  $\text{Fe}/\text{As}$  ratio of 2/1 was considered more appropriate to consistently achieve an effluent containing no more than 5.0 mg/L residual arsenic.

In all cases, the scaled up settling column tests produced equal or better arsenic reductions and/or residual arsenic concentrations, than had been attained by the corresponding jar tests when identical chemical dosages were used.

Relative settling rates of the primary floc for the ferric-lime process are shown in Figure 5 for different  $\text{Fe}^{+3}/\text{As}$  ratios. The sample selected for this illustration had an initial arsenic concentration of 320 mg/L. Relative settling rates for the first

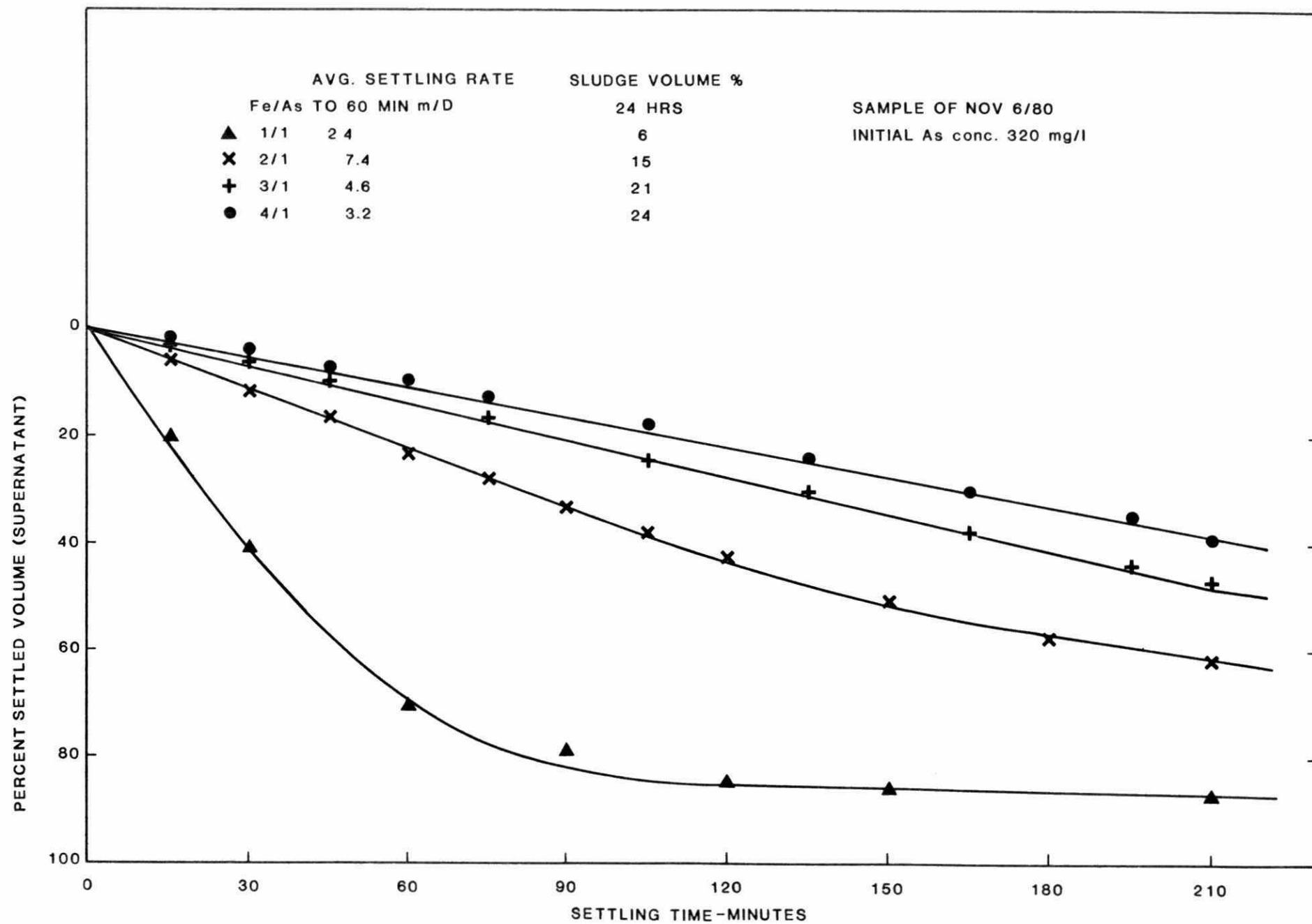


FIGURE 5 SETTLING CURVES FOR ARSENIC SLUDGE  $[As-FeCl_3-Ca(OH)_2]$

60 minutes of settling ranged from 24 m/d to 3.2 m/d when the Fe/As ratio was varied from 1/1 to 4/1, respectively. The settling rates are unique for this particular sample and will be different for samples having different initial arsenic concentrations at identical  $\text{Fe}^{+3}/\text{As}$  ratios. Generally, settling rate varies according to floc density and sludge volume which result from the combined action of the raw arsenic concentration and the selected  $\text{Fe}^{+3}/\text{As}$  ratio. The resulting sludge volumes following 24 hours of settling were 6, 15, 21 and 24% of the initial sample volumes for Fe/As ratios of 1/1, 2/1, 3/1 and 4/1, respectively.

#### ARSENIC SLUDGE CHARACTERISTICS

The characteristics of ferric-lime sludges, including dewaterability by centrifugation and arsenic release by leaching, are summarized in Table 7. All sludge characteristics presented here are based on sludges that have not undergone additional sludge conditioning such as polymer addition.

Table 7 illustrates that as the Fe/As ratio increases both sludge volume and mass increase. It was also observed during the study that as the Fe/As ratio increased, the resulting sludge became more gelatinous and retained more water after dewatering by centrifuge under identical conditions.

Analytical results of arsenic concentrations in the air dried sludge were found to be inaccurate. Consequently, all calculations relating to arsenic leachability were based on the total quantity of arsenic originally present in the liquid sample. This was a reasonable assumption since arsenic concentrations in the treated supernatant were always very low.

The data in Table 7 clearly indicated that the stability of arsenic in the sludges, increases with the  $\text{Fe}^{+3}/\text{As}$  ratio. In the November 6 sample, the amount of arsenic leached from the sludge with  $\text{NH}_4\text{Cl}$  solution decreased from 1,900  $\mu\text{g/g}$  of dried sludge to 770, 350 and 140  $\mu\text{g/g}$  as the  $\text{Fe}^{+3}/\text{As}$  ratio increased from 1/1 to 2/1, 3/1 and 4/1 respectively. The corresponding percentages of arsenic leached were 1.19, 0.71, 0.34 and 0.17%

TABLE 7

## ARSENIC SLUDGE CHARACTERISTICS

<u>Data Sampled</u>	<u>September 4/80</u>		<u>November 6/80</u>			
Raw Waste Sample Volume-L	30	30	25	25	25	25
Total As at Start-g	5.1	5.1	8.0	8.0	8.0	8.0
Fe <sup>+</sup> /As Ratio	1.2/1	4/1	1/1	2/1	3/1	4/1
Sludge Volume-% (24 hrs)	-	13	6	15	21	24
Total Solids, Settling Only-%	2.5 (5)*	1.25 (1)*	5.5 (16)*	3 (12)*	2.8 (9)*	3.1 (6)*
Weight of Wet Sludge Cake-g (1)	96	292	178	495	560	615
Moisture in Sludge Cake-%	68	83	72	85	86	84
Weight of Air Dried Sludge Cake-g	31	50	50	74	78	98
As in Air Dried Sludge-% (2)	17	8	23	14	11	9
As Leached with NH <sub>4</sub> Cl-μg/g (3)	1100	240	1900	770	250	140
As in NH <sub>4</sub> Cl Leachate - mg/L	47	10	81	33	15	6
As Leached with Water-μg/g (3)	480	180	660	500	180	120
As in Water Leachate-mg/L	21	8	29	22	8	5
% As Leached with NH <sub>4</sub> Cl-%	0.67	0.24	1.19	0.71	0.34	0.17
% As Leached with Water-%	0.29	0.18	0.41	0.46	0.18	0.15

$$\% \text{ As Leached from Sludge} = \frac{(\text{weight of As Leached}) (\text{weight of air dry sludge})}{(\text{weight of As at start})}$$

- (1) Centrifuged Sludge Cake  
 (2) Based on sludge analysis for total arsenic  
 (3) μg/g of As leached/g of dry sludge  
 \* Number in ( ) refers to days sludge has settled  
 Leaching time is 16 hours unless stated otherwise

respectively. Similarly, on September 4 arsenic leached with  $\text{NH}_4\text{Cl}$  solution decreased from 1,100 to 240  $\mu\text{g/g}$  or from 0.67% to 0.24%, as the  $\text{Fe}^{+3}/\text{As}$  ratio increased from 1.2/1 to 4/1, respectively.

Table 7 also shows that less arsenic was leached from the sludge cake with water than with  $\text{NH}_4\text{Cl}$  solution. Percentage arsenic leached from the sludge by distilled water ranged from 0.29 to 0.18 and 0.41 to 0.15 for samples obtained September 4 and November 6, respectively. Again, the lower values correspond to the higher  $\text{Fe}^{+3}/\text{As}$  ratio.

Whether or not, leachability of arsenic is affected by the percentage of arsenic in the dried sludge was not evaluated.

#### ONSITE PILOT PLANT STUDIES

The pilot plant results are summarized according to the process configuration under evaluation. The results are presented in Tables 8 and 9.

##### Two Stage Chemical Addition Nominal Fe/As Ratio 2/1

This process operating scheme was studied on four separate occasions. Study results are summarized in Table 8. On each occasion, a different set of retention times in the ferric, lime, polymer contact tanks, and final clarifier were studied. The retention times were altered by varying the raw waste feed rate and/or volume of the contact tanks. Fe/As ratio and final effluent pH were kept close to 2/1 and 9.6 to 10.9 respectively for all four occasions. Table 8 clearly illustrates that under the prevailing operating condition arsenic removals were consistently in excess of 99.0%. Corresponding residual arsenic concentrations in the treated effluent did not exceed 5.0 mg/L.

Table 8 further illustrates that under the prevailing operating condition, and particularly as long as the Fe/As molar ratio was kept very close to 2/1 and the final pH in the range of 9.0 to 12.0, arsenic removal efficiency was not affected to any observable degree by the relatively large variations in raw waste arsenic concentration. Similarly, the wide variations

TABLE 8

EFFECT OF MIXING TIME ON ARSENIC REDUCTION DURING PILOT PLANT OPERATION

TWO STAGE CHEMICAL ADDITION, NOMINAL Fe/As=2/1

Process Study Period		August 11-26		Sept. 17-18		Sept. 21-24		Sept. 14-16	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
Raw Waste Flow	L/min	13-18	13.5	15-20	15.8	19-25	20.9	26-30	29.3
Fe Tank, Contact Time	min.	8-12	11.5	4.8-6.0	5.2	2.4-6.9	4.1	1.9-4.5	3.1
Lime Tank, Contact Time	min.	21-31	29.6	13.8-16.7	15.2	8.0-18.6	11.8	7.3-10.8	8.4
Polymer Tank, Contact Time	min.	9-12	11.1	7.5-10	9.5	6.0-7.9	7.2	5.0-5.8	5.1
Clarifier, Contact Time	min.	25-37	35.2	24-32	30.0	19.0-25.0	23.0	16-30	24.0
Clarifier, Overflow Rate	m <sup>3</sup> /m <sup>2</sup> -day	-	44	-	52	-	68	-	96
Fe/As Molar Ratio	-	1.5-2.6	2.0	1.8-2.7	2.2	1.6-2.7	2.1	2.05-2.42	2.2
Lime Dosage	mg/L	820-2132	1171.0	1600-2353	2030	1080-1580	1354	1099-4533	2384
Polymer Dosage	mg/L	5.3-11.0	7.4	12.3-17.6	15.1	6.0-11.2	8.5	14.7-18.5	17.4
pH-Final	-	8.9-12.2	10.4	9.9-11.8	10.9	9.1-11.6	9.6	9.0-12.1	10.4
Lime Tank T.S.	%	0.35-2.64	1.11	0.6-0.74	0.68	0.44-0.57	0.5	0.77-1.01	0.9
Sludge-Final T.S.	%	1.9-3.0	2.8	2.1-4.4	3.4	1.65-5.12	2.9	1.21-3.10	1.9
As Conc., Raw Waste	mg/L	228-370	315	495-630	578	346-480	413	620-760	620
As Conc., Final Effluent	mg/L	1.0-3.4	2.4	1.5-5.0	2.9	0.8-4.5	1.5	1.8-3.5	2.8
As Removal	%	99.1-99.6	99.2	99.1-99.7	99.5	99.9-99.8	99.6	99.4-99.7	99.5
Polymer/Lime Tank SS Ratio	(wt/wt)	1/574-1/2495	1/1247	1/503-1/697	1/608	1/411-1/833	1/618	1/438-1/680	1/512
Polymer/Raw As Conc. Ratio	(wt/wt)	1/18-1/61	1/46	1/47-1/61	1/54	1/36-1/46	1/41	1/34-1/46	1/39
Lime/As Ratio	(wt/wt)	3/1 -5.3/1	3.7/1	2.7/1-4.2/1	3.5/1	2.7/1-3.9/1	3.3/1	1.7/1-6/1	3.4/1
# of Operating Days			7		2		4		3
# of Samples Analysed for As			13		6		21		10



in selected retention times for ferric chloride (1.9-12.0 min.), lime (7.3-31.0 min.) and polymer (5.0-12.0 min.) mixing and clarifier overflow rate ( $44-96 \text{ m}^3/\text{m}^2\text{-day}$ ) had no substantial effect on arsenic treatment efficiency. The importance of Fe/As molar ratio to arsenic removal efficiency will be further illustrated by Table 9 and discussed in the next section. Average lime dosage to raw arsenic concentration weight ratio was relatively constant at 3.3/1 to 3.7/1. Average polymer dosage to raw arsenic concentration weight ratio exhibited slight variations (1/39 to 1/54). Prevailing polymer dosage was based on visual observations of floc formation and settling characteristics in the final clarifier. For some unknown reason, total solids in the lime tank were abnormally high during August 11-26. As a result, the average ratio of polymer dosage to Fe/Lime floc density was very low at 1/1247. On the other three occasions, the average ratio of polymer dosage to Fe/Lime floc density (T.S. in lime tank) varied between 1/512 to 1/618. Total solids concentrations in the final sludge ranged from 1.9% to 3.4% which indicates the need for additional sludge thickening.

Operation without the addition of a polymer to the Fe/Lime floc was also evaluated occasionally (results not presented). According to visual observations, this mode of operation produced poor settling characteristics in the final clarifier resulting in substantial floc carryover.

Two Stage Chemical Addition - Nominal Fe/As Ratio 1/1

Results for this process August 27-28, are summarized in Table 9. With the exception of a lower Fe/As molar ratio (1/1), other operating conditions such as retention times, clarifier overflow rate, and final effluent pH were kept within the same ranges as for the other four test runs presented in Table 8. Although the data clearly illustrate that this process consistently attained arsenic removals in excess of 95%, it did not attain residual arsenic concentrations below 5.0 mg/L. It may be concluded that an Fe/As ratio of 1/1 does not provide sufficient margin for unexpected fluctuations in the prevailing raw arsenic concentration and/or compensate for any other process variable fluctuations. As expected, the lower Fe/As ratio required less lime for a final pH of 9.5 to 11.0 than when a Fe/As ratio of 2/1 was used. Polymer dosage was also very low for this process. This was of a direct consequence of the low Fe/As ratio which consequently produces a Fe/Lime floc of lower density.

One Stage Chemical Addition - Nominal Fe/As Ratio 2/1

The effectiveness of one stage chemical addition was studied August 31-September 1, and results are summarized in Table 9. For operating conditions similar to the two-stage chemical addition process, the single-stage chemical addition process did not consistently perform as well as the two-stage process. Treatment objectives of 95% arsenic removal and/or  $\leq 5.0$  mg/L arsenic residual were not obtained. For this reason, the process was not evaluated further.

TABLE 9

## SUMMARY OF PILOT PLANT OPERATION RESULTS

Process Study Period		Two Stage Chem. Add.- Fe/As=1/1, Aug. 27-28		One Stage Chem. Add.- Fe/As=2/1, Aug. 31- Sept. 1		High Density Fe/As=2/1 Sept. 2-3*	
		<u>Range</u>	<u>Mean</u>	<u>Range</u>	<u>Mean</u>	<u>Range</u>	<u>Mean</u>
Raw Waste Flow	L/min.	14.3-15.8	15.0	14.3-15	14.8	10-15	13.9
Fe Tank, Contact Time	min.	-	15	8-10	9	7.3-14.8	11
Lime Tank, Contact Time	min.	-	23	10-23	20	8.2-13.8	11
Polymer Tank, Contact Time	min.	-	10	-	10	-	11
Clarifier, Contact Time	min.	-	32	-	32	-	36
Clarifier, Overflow Rate	m <sup>3</sup> /m <sup>2</sup> -day	-	49	-	48	-	45
Fe/As Molar Ratio	L/min.	0.78-1.30	1.1	1.78-2.16	1.9	0.99-3.29	2.1
Lime Dosage	mg/L	527-827	691	1267-1678	1459	400-1920	1045
Polymer Dosage	mg/L	1.6-3.2	2.2	5.9-7.8	6.7	7.4-15.5	10.4
pH-Final	-	9.5-11.2	10.6	9.3-11.7	11.0	8.2-12.3	10.9
Lime Tank T.S.	%	0.22-0.24	0.2	0.41-0.43	0.4	0.24-2.52	1.0
Sludge -Final T.S.	%	-	-	-	-	0.15-7.05	-
As Conc., Raw Waste	mg/L	315-378	330	282-335	316	230-325	274
As Conc., Final Effluent	mg/L	5.3-10.0	7.7	3-24	6.6	1.5-4.4	2.3
As Removal	%	97-98	97.3	92.7-99.2	97.9	98.2-99.5	99.2
Polymer/Lime Tank SS Ratio	(wt/wt)	1/1100-1/1200	1/1147	1/551-1/612	1/592	1/209-1/2250	1/998
Polymer/Raw As Conc. Ratio	(wt/wt)	1/101 -1/236	1/152	1/40 -1/57	1/48	1/17 -1/33	1/28
Lime/As Ratio	(wt/wt)	1.6/1 -2.6/1	2.1/1	3.8/1 -5.3/1	4.6/1	1.2/1 -7.2/1	3.5/1
# of Operating Days			2		2		2
# of Samples Analysed for As			10		10		17

\* Contact times and overflow rate based on raw waste flowrate. Average sludge return to lime tank was 12/8 L/min. or about 92%.

### High Density Process

Results for the high density process are summarized in Table 9. With the exception of sludge recirculation, at a rate of about 92% of the raw waste feed rate (volume basis), other operating conditions were similar to the two-stage process at a Fe/As ratio of 2/1. This process was tried because it had been successfully employed in a similar treatment (3) to provide nuclei for flocculation. On some occasions, Fe/Lime floc concentrations in the lime tank were substantially higher than without sludge recirculation. However, due to operating problems with sludge recirculation, mean total solids concentration in the Fe/Lime sludge did not exceed 1.0%. The higher Fe/Lime sludge total solids also required more polymer for effective subsequent flocculation. Average polymer to raw arsenic waste concentration ratio of 1/28 was substantially higher for this process as compared to the previously discussed processes. Lime dosage to raw arsenic concentration ratio was not significantly affected by sludge recirculation. Residual arsenic concentrations of less than 5.0 mg/L or removal efficiencies of 98.0% or better were consistently obtained throughout the study period. Due to operating problems, and also the anticipated higher polymer dosage requirements, the high density process was not advanced for additional evaluation. Furthermore, the prevailing high solids concentrations did not suggest that sludge recirculation was required except during the start-up phase.

- (3) Winter, E.F., Garritsen, P.G., Butler, H.R., Effluent Treatment at Inco's Port Colborne Nickel Refinery. Paper presented at the 28th Ontario Industrial Waste Conference, June 14-17, 1981, Toronto.

#### PILOT PLANT VS BENCH-SCALE RESULTS

Results from pilot plant operation at a nominal Fe/As ratio of 2/1 and two-stage chemical addition agreed well with bench-scale studies at an Fe/As ratio of about 1/1 or higher. Similar to bench-scale studies, changes in retention times, within the ranges studied for ferric, lime and polymer, had no significant effect on the overall process. During the study period, both at the pilot and bench-scale levels, an Fe/As ratio of 2/1 was at all times sufficient to attain the required treatment objectives under the prevailing raw arsenic concentrations of 170-750 mg/L As.

No detrimental effects toward the treatment process due to overdosing with ferric, lime or polymer were observed during the bench-scale studies. It is realized, however, that chemicals may be wasted at a fixed ferric feed rate together with the production of unnecessary quantities of sludge.

## CONCLUSIONS

### Design of Fullscale Treatment Plant

To consistently meet the treatment plant objectives, the two-stage chemical addition process at a nominal Fe/As molar ratio of 2/1 is recommended. A five minute mixing time is considered adequate for this phase of the process.

In a separate mixing tank, lime should be added to attain a final pH within a range of 9.0 to 11.0. Lime/As weight ratio of about 3/1 with a ten minute mixing time is necessary.

Secondary flocculation with a suitable polymer at an average polymer/raw arsenic weight ratio of 1/45 at about five minutes slow mixing is also required.

A workable clarifier overflow rate is in the order of  $50 \text{ m}^3/\text{day-m}^2$ .

Based on the above design parameters, the retained consultant has designed a  $460 \text{ m}^3/\text{day}$  arsenic treatment plant which is presently near completion at the Deloro site.

APPENDIX

PROCESS DEFINITIONS

Conventional two-stage process (also referred to in this report as two-stage chemical addition), implies that ferric chloride and lime are sequentially dosed to the waste stream in two separate reaction tanks, respectively.

Conventional one-stage process (also referred to in this report as one-stage chemical addition) implies that both ferric chloride and lime are dosed simultaneously to a single reaction tank.

High density process is similar to the two-stage process with the exception that waste sludge is recirculated to the lime tank.

In all cases, Fe/As ratios denote molar ratios. The chemicals symbols  $\text{Fe}^{+3}$  and/or Fe are used interchangeably.

RURAL RUNOFF POLLUTION  
AND  
CONTROL OPTIONS

by

S.N. Singer, J. Arnold, W.T. Dickinson,  
A.F. Smith and S.K. So

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Rural Runoff Pollution  
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Control Options

S. N. Singer, J. Arnold, W. T. Dickinson, A. F. Smith,  
and S. K. So

ABSTRACT

In Ontario, a large number of studies on agricultural nonpoint source pollution have been carried out by various government agencies and research institutions. These studies have established that agriculture contributes sediment, nutrients, other chemicals and bacteria to receiving waters at levels higher than those accounted for by natural processes. Several techniques and models have been developed and/or applied in Ontario to address the definition and quantification of agricultural nonpoint source pollution and to evaluate proposed remedial measures. The results of the application of these techniques and models have been promising; however, further refinements are still necessary.

Control of nonpoint source pollution from agricultural land is a difficult problem and it poses an important public challenge. For control measures to be successful they must meet the test of being practical, economical, cost-effective and site-specific. The implementation strategy for agricultural control measures should emphasize erosion control, priority areas and supportive programs which include a combination of technical assistance to farmers, economic incentives, education and research.

## 1. INTRODUCTION

Interest in nonpoint sources of pollution from agricultural and urban areas has increased substantially in recent years as discharges from municipal and industrial areas have come under increasing control. In Ontario, a large number of studies on agricultural nonpoint sources have been and are being carried out by various government agencies and research institutions. Results from these studies have sharpened our awareness of the key issues of agricultural nonpoint source pollution and increased our understanding of the difficulties we face in bringing this pollution under control. Thus, it is timely to share some thoughts based on our experience of the past few years.

## 2. MAJOR STUDIES OF AGRICULTURAL NONPOINT SOURCE POLLUTION IN ONTARIO

### 2.1 Pollution from Land Use Activities Reference Group (PLUARG) Program

One of the most extensive studies of agricultural nonpoint sources of pollution in the Great Lakes basin, in general, and in Southern Ontario, in particular, was completed by PLUARG in 1978 under the Canada-U.S. agreement on Great Lakes Water Quality (IJC, 1978). A number of small watersheds representative of agricultural regions in Ontario were studied under PLUARG. The objectives of this investigation were to evaluate the effects of nonpoint sources (NPS) on the Great Lakes, to determine the causes of this pollution, and to propose remedial measures to alleviate it. During the investigation an attempt was made to relate water quality at the outlets of watersheds to specific land use and agricultural practices within these watersheds (Hore and Ostry, 1978).

The PLUARG final report indicated a significant agricultural contribution to water quality degradation in the Great Lakes. PLUARG, however, did not attempt to assess the impacts of agricultural NPS on local water quality. In spite of this shortcoming, many of the PLUARG findings are of great value to the

understanding of the NPS problems. PLUARG's extensive data base provides researchers and decision-makers with a wealth of information on the impacts of agriculture on water quality.

Since PLUARG was completed in 1978, a number of important watershed studies with a considerable agricultural NPS component have been carried out in Ontario. Various government agencies, research institutions, consulting firms, and farm organizations have been working together in close co-operation to develop sensible, economical and efficient strategies for managing agricultural NPS. Prominent among the studies are: the Grand River Basin Water Management Study, the South Nation River Basin Development Study, the Thames River Basin Water Management Study, the Stratford-Avon River Environmental Management Project, and the Lake Simcoe Environmental Management Study.

## 2.2 The Grand River Basin Water Management Study

The objectives of the agricultural NPS study in the Grand River basin were to investigate how natural land forms, agricultural land use, and agricultural practices affect the pollution loads to the river; to estimate future loadings based on projections of land use for the years 2001 and 2031; to identify remedial measures which could be implemented to reduce these loadings; and to evaluate the costs and effectiveness of these measures.

The Grand River Implementation Committee (GRIC, 1982) concluded that largely due to agricultural activities, the rural areas in the basin are the largest sources of sediment, nutrients and some heavy metals. Over 70% of such inputs occur during the spring runoff. Localized high levels of bacteria occur mainly in the summer from various livestock and feedlot operations. The present major agricultural NPS pollution areas are in the sub-basins of Canagagigue Creek, Conestogo River, middle Grand River (West Montrose to Brantford), and the Nith River (Figure 1). These areas represent the more intensively developed agricultural sub-basins of

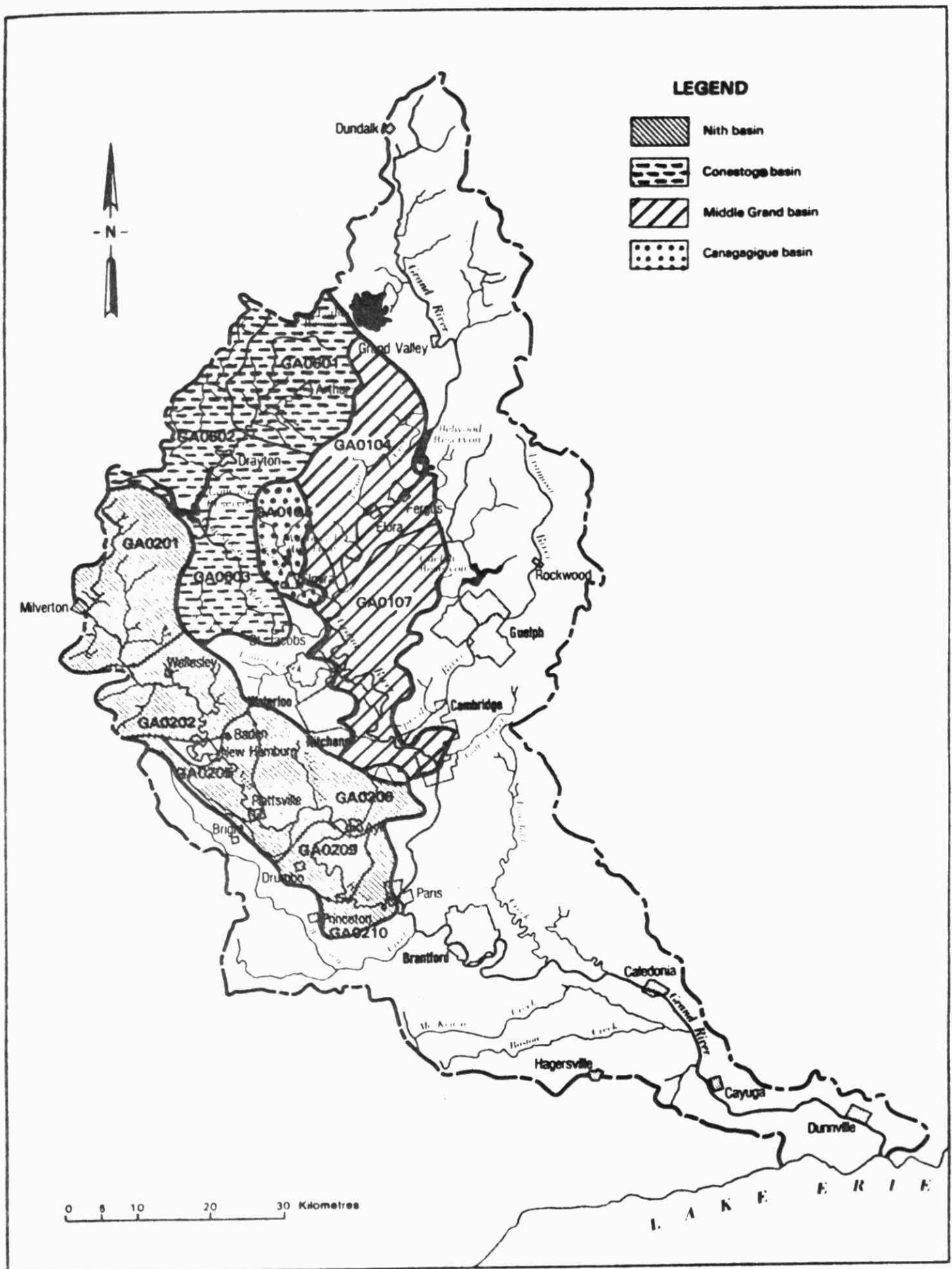


Figure 1. Major sub-basins contributing to agricultural nonpoint source pollution in the Grand River basin (GRIC, 1982).

the watershed. The recommended agricultural NPS control measures are:

- a) conservation tillage and no-tillage practices where applicable,
- b) stream bank stabilization,
- c) restriction of floodplain use to hay and pasture,
- d) restriction of cattle access to streams,
- e) establishment of buffer strips adjacent to watercourses, and
- f) land management practices which reduce soil erosion such as winter cover crops, contour cropping, grassed waterways, etc.

It is anticipated that the above control measures will result in benefits to the farmer with savings in soil, fertilizer and time; and benefits to the river with improvements in water quality. The method used in the analysis is discussed in Section 4.2.

### 2.3 The South Nation River Basin Development Study

The South Nation River Study was initiated in 1980 in order to formulate policy options and alternatives which deal with three serious water management problems: large annual floods during spring snowmelt, lack of summer flow, and poor water quality. A major concern in this study has been that outlet drains which are hydraulically efficient channels may aggravate downstream flooding. It is also suspected that agricultural tile and outlet drains individually and/or collectively may cause a further reduction in the already critical low-flow conditions in the South Nation River. In so doing, agricultural drainage could affect the existing water and sewage works and limit new opportunities (e.g. water supply, sewage works, irrigation, recreation, etc.) which are dependent on flows.

Preliminary findings indicate that land slides, open channel drains and sheet erosion of fields are the three major sediment producing

sources in the South Nation River basin. Cattle access to the streams, feed lot runoff and poor manure management are the likely sources of high phosphorus and bacteria levels in the river (MacLaren, Draft, 1982). The final report on the effects of various land use changes, agricultural drainage practices and water management alternatives is still under preparation.

#### 2.4 The Thames River Basin Water Management Study and The Thames River Implementation Committee

The Thames River Implementation Committee (TRIC) was formed in 1976 to implement the recommendations of the Thames River Basin Water Management Study. A major effort of TRIC was directed at improving agricultural land management in order to reduce the adverse impacts of agricultural diffuse sources. The TRIC program consisted of four main components:

- a) determination of priority land management areas,
- b) development of land management demonstrations,
- c) development of drain construction guidelines and applications, and
- d) initiation of a public information and education program.

Modelling techniques were used in TRIC to identify areas of high, medium and low erosion potential and areas of high, medium and low sediment yields to receiving streams (see Section 4.4).

TRIC initiated 45 demonstration projects which are, at present, in various stages of planning and/or implementation. These projects deal with problems due to sheet, rill, gully and bank erosion. The TRIC program provided subsidies to co-operating farmers for the initiation of erosion control programs. Figure 2 shows the locations of various demonstration sites within the Thames River basin. Also included on this figure are locations of "passive" demonstrations where good land management practices were already in place.





TRIC activities associated with drain construction guidelines included the development of a "Practical Guide for Municipal Drains" and also the establishment of drain construction demonstrations to display types of equipment, materials and methods for drain construction and maintenance.

TRIC's information and education program was extremely successful. Through meetings, displays, monthly news releases, a quarterly newsletter, "The Talk of The Thames", and the development of guidelines on municipal drains, agricultural erosion control, and fertilizer, pesticide and waste management, TRIC was able to disseminate information to basin residents (TRIC, 1982).

## 2.5 The Stratford-Avon River Environmental Management Project

The Stratford-Avon study was initiated in 1980, in an effort to resolve water quality problems in the Avon River. Earlier studies (MOE, 1979) suggested that satisfactory water quality levels could only be achieved through combined efforts in the areas of improved municipal waste treatment, agricultural runoff control and, possibly, the use of instream treatment methods. The specific objectives of the agricultural component of the Avon River Study have included the evaluation of the contribution of pollution loads from existing agricultural practices in the Avon River Watershed; development of land management demonstrations; and the assessment of the costs, benefits and applicability of specific remedial measures.

It was determined at the beginning of the Avon River study that localized demonstrations would best serve to assist farmers in overcoming resistance to new ideas. At present, 18 demonstration projects are being evaluated in the Avon River basin. These projects include:

- a) conservation vs. conventional tillage practices,
- b) strip cropping practices,
- c) controlled livestock access,
- d) improved drain construction,



- e) grassed waterways, and
- f) other erosion control measures such as drop inlet structures and sediment basins.

Modelling techniques were used extensively in the Avon River study to evaluate soil erosion, the effectiveness of controls and the impact of alternative crop and soil management practices on potential soil loss and sediment delivery. Further information on the results will be presented in Section 4.

## 2.6 The Lake Simcoe Environmental Management Strategy Studies

These studies were initiated in 1981 in order to upgrade the water quality in Lake Simcoe. The key to achieving this goal is the reduction of phosphorus loadings to the lake. Major components of these studies include the identification of phosphorus sources from agricultural lands in the Lake Simcoe Basin; and the evaluation of possible control measures. These studies are just underway with expected completion in 1984. (Lammers et al, 1982).

## 3. POLLUTION FROM AGRICULTURAL RUNOFF

Modern agricultural practices employ technologies which involve the use of fertilizers, pesticides, irrigation systems, improved drainage and confined livestock operations. A possible consequence is the increased potential for water quality degradation of receiving waters.

The quality of agricultural runoff reflects the type of soluble material with which the water comes in contact and the suspended materials it carries. Major pollutants from agricultural lands include sediment, nutrients, pesticides, organic matter and bacteria.

Estimates of pollutant contribution to surface waters from various nonpoint sources are provided in Table 1 (Sonzogni et al, 1980). Although this table offers insight into the relative significance of different sources, it does not tell the whole story. The concern is

TABLE 1. Ranges of Unit Area Loads by Land Use, kg/ha/year (After Sonzogni et al, 1980).

Land uses	Suspended Solids	Total phosphorus	Filtered reactive phosphorus	Total Nitrogen	Lead	Copper	Zinc	Chloride
Rural								
General agriculture	3-5600	0.1-9.1	0.01-0.6	0.6-42	0.002-0.8	0.002-0.9	0.005-0.3	10-120
Cropland	20-5100	0.2-4.6	0.05-0.4	4.3-31	0.005-0.006	0.014-0.064	0.026-0.083	10-50
Improved pasture	30-80	0.1-0.5	0.02-0.2	3.2-14	0.004-0.015	0.021-0.038	0.019-0.172	-
Forest/wooded	1-820	0.02-0.67	0.01-0.10*	1-6.3	0.01-0.03	0.02-0.03	0.01-0.03	2-20
Idle/perennial	7-820	0.02-0.67	0.01-0.07	0.5-6.0	0.01-0.03	0.02-0.03	0.01-0.03	20-35
Sewage sludge	-	0.2	0.01	11	0.01	0.005	0.2	10
Wastewater spray irrigation	-	0.2-1.4	0.1-1.3	370	-	-	-	-
Urban								
General urban	200-4800	0.3-4.8	0.05-0.4	6.2-18	0.14-0.5	0.02-0.21	0.3-1.0	130-750
Residential	620-2300	0.4-1.3	0.2	5-7.3	0.06	0.03	0.02	1050
Commercial	50-830	0.1-0.9	0.02-0.08	1.9-11	0.17-1.10	0.07-0.13	0.25-0.43	10-150
Industrial	450-1700	0.9-4.1	0.3	1.9-14	2.2-7.0	0.29-1.3	3.5-12.0	75-160
Developing urban	27 500	23	0.1	63.0	3.0	-	-	-

Dash (-) indicates data not available.

\*Total dissolved phosphorus.

not with loadings per se; rather the concern rests with those situations in which the loadings and the resulting concentrations exceed the assimilative capacity of the receiving water. This capacity depends on such time-variable components as streamflow, temperature, sunlight and pollution concentrations. The stochastic nature of most of these variables and the uncertainty that surrounds what we do know about the receiving water processes are indicative of the complexity of the agricultural NPS problem (Bailey and Waddel, 1979).

### 3.1 Sediment

Sediment generated by water or wind erosion is by far the most important water pollutant from agriculture (IJC, 1980). The detrimental effects of sediment include obstruction of drainage channels, filling of reservoirs, deterioration of aquatic habitat and decrease of recreational value. A major impact of sediment as a pollutant, however, is related to its ability to serve as a vehicle to carry other pollutants such as nutrients, pesticides, and heavy metals into receiving waters.

In Ontario, agricultural practices that leave the soil relatively bare during the snowmelt period contribute heavily to suspended sediment yields. Approximately 75% of the annual suspended sediment yield is transported in February, March and April (Wall et al, 1982).

During PLUARG, 11 small agricultural watersheds representative of major soils, crops, and livestock combinations were monitored and studied in southern Ontario. Unit area yields of suspended sediments from these watersheds ranged from less than 100 to 1000 kg/ha/year in a 2-year study. Bank erosion was estimated to contribute between 0 and 30% of the suspended sediments while cropland sheet and rill erosion was estimated to contribute 70-100% (Wall et al, 1982).

Regression analyses relating watershed characteristics to unit-area yields showed that percent clay in the surface soil and percent area

in row crops were the the most significant factors in estimating sediment yield (Wall et al, 1982; So and Singer, 1982).

### 3.2 Nutrients

Major nutrients, phosphorus and nitrogen, are introduced on agricultural lands from natural sources or through the application of fertilizers and animal wastes.

When nutrient levels in the soil surpass crop requirements, a portion of the excess nutrients become available to be carried away from the fields by surface runoff or to be leached into ground water aquifers. Animal wastes are a major potential source of water quality degradation because they contain high levels of nutrients, excessive organic matter and bacteria.

#### 3.2.1 Phosphorus

High levels of phosphorus induce nuisance growth of aquatic plants. When present in abundance, aquatic plants interfere with the recreational use of a waterbody. Through respiration or due to death and decay, aquatic plants deplete the oxygen levels in the water and render it unsuitable for domestic and industrial supplies, unfit as a fish habitat, and unattractive for recreation.

Ontario research has found that approximately 60% of the total phosphorus in runoff is associated with sediment (Miller and Spires, 1978). The total Canadian agricultural contribution to the Great Lakes basin has been estimated by PLUARG to be 3000 t/year, of which 40% is in dissolved and readily available forms. The PLUARG studies indicated that about 70% of this load was attributable to cropland runoff, 20% to livestock operations, and 10% to a combination of unimproved land and streambank erosion (Miller et al, 1982). Unit-area loads from the 11 agricultural watersheds studied under PLUARG in southern Ontario range from 0.03 to 1.79 kg/ha/year for total phosphorus and from 0 to 0.49 kg/ha/year for filtered reactive phosphorus.

Regression analyses on PLUARG data showed that percent clay in surface soil and percent area of row crops were significant in explaining the variability in total phosphorus unit-area loads. Percent clay in surface soil and the total phosphorus applied (fertilizer + manure) were the most important variables in explaining the unit-area loads of filtered reactive phosphorus (Miller et al, 1982).

### 3.2.2 Nitrogen

Dobson et al (1974) and Neilsen et al (1978) concluded that lake eutrophication due to nitrogen is not a problem in the Great Lakes and that nitrogen is rarely a limiting factor for aquatic plant growth. In farmland, however, excessive application of nitrogen fertilizers may result in contamination of ground water supplies. Concentrations of nitrate and nitrite in excess of 10 mg/L in drinking water constitute a health hazard. The nitrite form of nitrogen is particularly toxic because it interferes with the process of oxygen transport in the blood. Ontario drinking water quality criteria (MOE, 1978) require that the public be warned of the potential dangers of using water for infant feeding in areas where the nitrate content is known to be in excess of 10 mg/L. High concentrations of nitrates which exceed MOE drinking water criterion have been reported in a number of water wells in various locations in Ontario (Vallery et al, 1982). The reasons for the high concentrations have not been investigated, however, most are likely attributable to agricultural activities.

Ontario provincial water quality objectives (MOE, 1978) require that concentrations of un-ionized ammonia should not exceed 0.02 mg/L for the protection of aquatic life. Surface waters in the immediate vicinity of a feedlot can become contaminated by ammonia and a fish kill may result. A number of fish kills caused by liquid manure mainly from pig operations occur annually in southwestern Ontario (J. Westwood, MOE, London, Ontario, personal communication).

Neilsen et al (1982) summarized PLUARG findings on total Kjeldahl nitrogen (TKN) and total nitrate nitrogen ( $\text{NO}_3\text{-N}$ ) from the 11 agricultural watersheds in southern Ontario. They reported that the total nitrogen unit-area loads range from 3.5 to 29.2 kg/ha/year and that 75% of these loads are in the form of  $\text{NO}_3\text{-N}$ .

Total nitrogen and  $\text{NO}_3\text{-N}$  unit-area loads were found to be significantly correlated with total nitrogen addition to the watershed (fertilizer + manure N) as well as with percent of watershed under cultivation in row crops or tile-drained. The TKN unit-area loads were positively correlated with surface soil clay content (Neilsen et al, 1982).

### 3.3 Pesticides

Four major categories of pesticides are used in agriculture: fungicides, herbicides, insecticides and nematocides. Their use has risen substantially during the past decade because they improve the quality of produce and increase yields.

Organochlorine insecticides, and DDT in particular have been shown to cause environmental problems such as accumulation in fish and reproductive failures in fish-eating birds (Nicholson and Hill, 1970). DDT was banned in Ontario in 1972 and the organochlorine compounds have generally been replaced by organophosphorus and carbamate insecticides. Frank et al (1982) indicate that among the pesticides used in Ontario, only atrazine, endosulfan and simazine persisted long enough to appear in water throughout the year but there has been no evidence of environmentally related problems.

Frank et al (1982) summarized the findings of PLUARG in the 11 agricultural watersheds in southern Ontario. The study revealed that 81 pesticides were applied to farms and rights-of-way during 1975 in Ontario. An average of 39% of the land surface in the 11 watersheds was treated with a mean rate of 8.27 kg/ha of pesticides. The application rate varied from 0.005 kg/ha on hay and pasture to 51 kg/ha on potatoes, tomatoes, and tobacco.

Pollution from the entry of pesticides into stream water can be caused by surface runoff (60%), internal soil drainage (18%) and spills due to carelessness associated with operating equipment adjacent to streams (22%) (Frank et al, 1982). Spills of pesticides caused a number of fish kills in southwestern Ontario streams (J. Westwood, personal communication).

#### 4. TECHNIQUES AND MODELS TO EVALUATE AGRICULTURAL POLLUTION AND CONTROL OPTIONS.

Several techniques and models have been developed in recent years to address the definition and quantification of agricultural NPS pollution and to evaluate proposed remedial measures. In this section, an attempt will be made to summarize our experience in Ontario.

##### 4.1 Regression Models

The thrust of the PLUARG effort was to determine comparative sources of unit-area loadings. Regression models involving watershed land use and physiographic characteristics as independent variables, and instream water quality parameters as dependent variables were used extensively. For example, a regression equation was developed for the prediction of suspended sediment load. The watershed variables considered in the analysis included: percent clay and sand, available P, fertilizer P, manure, total P added, percents hay and pasture, alfalfa, woodland, rowcrops, corn, animal units, rural residences, and stream density. The developed equation is of the form:

$$Y = -204 + 7.9 (\% \text{ row crop}) + 11.0 (\% \text{ clay})$$

$$R^2 = 0.64$$

Wall et al (1982)

where Y is the predicted sediment yield, kg/ha/year. This relationship explains 64% of the total variation in the sediment yield data (i.e.,  $R^2 = 0.64$ ).



#### 4.2 Analysis Method Used in the Grand River Study

A quantitative-qualitative method which explains the measured pollutant loads in terms of natural background conditions, land use, and agricultural practices was successfully applied to the Grand River Basin (So and Singer, 1982). The method proceeds as follows:

1. Identify the causes of agricultural pollution in the watershed in terms of land form characteristics, land use and agricultural practices.
2. Rank the identified causes of pollution in terms of significance.
3. Rank the pollutant loads measured at the outlet of the watershed into different levels.
4. Determine three indices for the watershed:
  - a) present Pollution Index based on measured pollutant loads,
  - b) natural Pollution Index based on natural land form characteristics, and
  - c) agricultural Land Use and Practices Index based on present agricultural land use intensity and management practices.

For the Grand River Basin Water Management Study, a scoring system was used to rank the relative significance of various causes of agricultural pollution and the different levels of pollutant loads. The scoring system used was subjective with the scores assigned to each case ranging from 1 or 2 for small loads or insignificant causes to 3 or 4 for large loads or significant causes (Table 2). The pollution indices identified for various sub-basins in the Grand River watershed (Table 3) were used as the basis for the identification of remedial measures and costs (Tables 4 and 5).



TABLE 2. Weighting Scores Used in the Grand River Basin Water Management Study (So and Singer, 1982).

Parameter	Range	Scores
Suspended solids, kg/ha/year	< 200	1
	200-400	2
	400-600	3
	> 600	4
Total phosphorus, kg/ha/year	< 0.3	1
	0.3-0.6	2
	0.6-0.9	3
	> 0.9	4
Filtered reactive phosphorus kg/ha/year	< 0.07	1
	0.07-0.14	2
	0.14-0.21	3
	> 0.21	4
Total Kjeldahl nitrogen kg/ha/year	< 2.0	1
	2.0-3.0	2
	3.0-4.0	3
	> 4.0	4
Filtered nitrite and nitrate kg/ha/year	< 5.0	1
	5.0-10.0	2
	10.0-15.0	3
	> 15.0	4
Potential for soil erosion	Low	1
	Moderate	2
	High	3
	Very high	4
Topography	Level	1
	Gently Sloping	2
	Rolling	3
	Hilly	4
Stream bank conditions	None or occasional problem	1
	Minor problem	2
	Moderate problem	3
	Major problem	4

TABLE 2 - continued

Parameter	Range	Scores
Natural buffer strips	Adequate in all locations	1
	Adequate in most locations	2
	Adequate in some locations	3
	Inadequate	4
Row crops, % of sub-basin area	< 10.0	1
	10.0-20.0	2
	20.0-30.0	3
	> 30.0	4
Livestock operations animal units/ha	< 0.3	1
	0.3-0.5	2
	0.5-0.8	3
	> 0.8	4
Flood plain cropping	None or occasional	1
	Minor problem	2
	Moderate problem	3
	Major problem	4
Cattle access to streams	None or occasional	1
	Minor problem	2
	Moderate problem	3
	Major problem	4
Conventional tillage	No tillage	1
	Minimum tillage	2
	Conservation tillage	3
	Conventional tillage	4

TABLE 3. Natural Pollution Potential, Agricultural Land Use and Practice Level, and Present Pollution Levels for 19 Sub-Basins in the Grand River Basin (So and Singer, 1982).

Sub-basin	Area ha	Natural Pollution Potential	Agricultural Land Use and Practice level	Present Pollution level
Upper Grand R. GA0101 & GA0102	68898	High	Low	Low
GA0103	13400	High	Medium	Low
Middle Grand R. GA0104	36752	Medium	Low	Medium
GA0107	38376	Medium	Medium	Medium
Lower Grand R. GB0102	46399	Low	Medium	Low
Canagagigue Cr. GA0105 & GA0106	10761	High	High	High
Conestogo R. GA0601	27707	High	Medium	High
GA0602	28829	Medium	High	Medium
GA0603	21000	Medium	High	High
Speed R. GA0401	5705	Medium	Medium	Low
GA0402	22148	Medium	Low	Low
GA0408	13682	Medium	Low	Low
Eramosa R. GA05	26505	Medium	Low	Low
Aberffoyale Cr. GA0301 & GA0304	9261	Low	Low	Low
Nith River GA0201	32363	High	High	High
GA0202	21900	Medium	High	High
GA0205-GA0210	57569	Medium	High	High
Whiteman Cr. GB0501	38115	Medium	Medium	Medium
McKenzie Cr. GB0201	20297	Medium	Low	Medium

TABLE 4. Major Causes of Agricultural Non-Point Source Pollution and Proposed Remedial Measures for Sub-Basins with Intensive Agricultural Development in the Grand River Basin (So and Singer, 1982).

Sub-basins	Major Causes of Non-Point Source Pollution	Remedial Measures
<u>Middle Grand River</u>		
1. Sub-basin GA0104	1. Stream bank erosion in Irvine Creek 2. Inadequate buffer strips	1. Stream bank stabilization 2. Widen buffer strips
2. Sub-basin GA0107	1. Stream bank erosion along Cox Creek 2. Cattle access to Hopewell Creek 3. Floodplain cultivation of crops along Hopewell Creek	1. Stream bank stabilization 2. Fencing to restrict cattle access to streams 3. Replace cultivation of row crops in the floodplain with hay crops and pasture
<u>Canagagigue Creek</u>		
1. Sub-basins GA0105 and GA0106	1. Stream bank erosion 2. Inadequate buffer strips 3. Probable cattle access to streams 4. Trout farm	1. Stream bank stabilization 2. Widen buffer strips 3. Fencing to restrict cattle access to streams
<u>Conestogo River</u>		
1. Sub-basin GA0601	1. Stream bank erosion 2. Inadequate buffer strips 3. Cattle access to streams	1. Stream bank stabilization 2. Widen buffer strips 3. Fencing to restrict cattle access to streams
2. Sub-basin GA0602	1. Stream bank erosion 2. Inadequate buffer strips 3. Cattle access to streams	1. Stream bank stabilization 2. Widen buffer strips 3. Fencing to restrict cattle access to streams
3. Sub-basin GA0603	1. Stream bank erosion 2. Inadequate buffer strips 3. Cattle access to stream	1. Stream bank stabilization 2. Widen buffer strips 3. Fencing to restrict cattle access to streams
<u>Nith River</u>		
1. Sub-basin GA0201	1. Stream bank erosion 2. Inadequate buffer strips 3. Cattle access to stream	1. Stream bank stabilization 2. Widen buffer strips 3. Fencing to restrict cattle access to streams
2. Sub-basin GA0202	1. Stream bank erosion 2. Inadequate buffer strips 3. Floodplain cultivation of crops	1. Stream bank stabilization 2. Widen buffer strips 3. Replace cultivation of row crops in the floodplain with hay crops and pasture
3. Sub-basins GA0205, GA0206, GA0209 and GA0210	1. Stream bank erosion 2. Inadequate buffer strips 3. Floodplain cultivation of crops	1. Stream bank stabilization 2. Widen buffer strips 3. Replace cultivation of row crops in the floodplain with hay crops and pasture

TABLE 5. Costs and Benefits of Rural Non-Point Source Controls  
(Present Value of Costs in Millions of 1979 Dollars at 6% Discount),  
(So and Singer, 1982).

Action	Costs (Million \$)	Benefits to Farmers	Water Quality Benefit
Conservation tillage	varies	- labour, time, fertilizer, sustaining crop yields, retain topsoil	reduces sediment and nutrient loading
Stream Bank Stabilization	1.5	- reduces annual costs of ditches to farmer, reduces loss of adjacent farmland due to gullyng, etc. protects tile outlets	reduces sediment loading and nutrient loading (5 to 30 percent)
Floodplain Management	3.6	- saving of topsoil	reduces sediment and nutrient loading (10 to 20 percent)
Restriction of cattle acces to stream and ditches	0.3	- prevent destruction of banks, reduces cost of bank maintenance, prevents associated loss of farmland	reduces sediment, nutrient and bacteria loading (5 to 10 percent)
Buffer strips	0.8	- along ditches and streams - a buffer strip is an integral part of ditch structure and as such helps protect ditch banks, reduces water velocity.  - along field boundaries buffer strips create opportunity for tree windbreaks.	reduces sediment and nutrient loading to stream (5 to 10 percent)
TOTAL	5.48		

#### 4.3 HSP-F and DRAINMOD Models

Two models were used in the study of water resources of the South Nation River basin. These models are the "Hydrological Simulation Program - Fortran" (HSP-F) and the DRAINMOD model. The HSP-F model was selected to examine the impacts of various land use scenarios, including that of agricultural land drainage on basin hydrology for untilled conditions. The DRAINMOD model was used to simulate tile drainage conditions (MacLaren, Draft, 1982).

In its draft report on the South Nation River Basin Study, MacLaren Ltd. reported that the combined HSP-F and DRAINMOD models can realistically reproduce the impacts of improved outlet drains and tile drain installation as a result of investigation on small test areas. It was also shown that the HSP-F model alone can be adjusted to reproduce these results as a lumped model. The way is now clear to apply these conclusions to the watershed model to determine the impacts of agricultural drainage improvement on the watershed as a whole (McLaren, Draft 1982).

#### 4.4 Computerized Universal Soil Loss Equation, GAMES and ANSWERS Models

Three models were applied in the Avon River basin study and two of these models were applied in the Thames River Study. The Universal Soil Loss Equation (USLE), presented by Wischmeier and Smith (1965) to describe sheet and rill erosion, was the main loading function used in these models to assess soil losses in the basins and to evaluate the impact of alternative management practices.

##### 4.4.1 Computerized USLE Model

A screening of erosion prone areas in the Avon River watershed was conducted by the Lands Directorate of Environment Canada using the USLE. The watershed was divided into polygons ranging in size from 10 to 200 acres. Factors such as rainfall energy, slope, slope length, soil erodibility, and crop cover were

identified for each polygon and the annual gross erosion per unit area was computed for each polygon (Figure 3). A sediment delivery coefficient and loading functions for total phosphorus and filtered reactive phosphorus were computed based on data collected at a federal monitoring station located below the City of Stratford.

The annual gross erosion from the Avon watershed was estimated to be approximately 86,000 tonnes; delivered sediment to the river 15000 tonnes; total phosphorus 6.2 tonnes, and filtered reactive phosphorus 1.2 tonnes (Coleman, Draft 1981). Over 60% of the erosion was estimated to occur in areas of intensive agriculture including corn and bean monocultures, corn and bean rotational systems and field vegetables. Gross erosion per unit-area appeared highest for steeply-sloped fields with intensive agriculture (Table 6).

A number of control options were evaluated in terms of erosion reduction (Table 7). The most substantial gains could be made on slopes above 2% using cross-slope or contour farming in areas with intensive agriculture. The greatest absolute reduction could be achieved on slopes of 7-12% followed closely by slopes of 2-7% (Coleman, Draft, 1981).

The same USLE model was applied to the Thames River basin. The model made it possible to identify areas in the basin with high, medium and low gross erosion potential (Figure 4). Results of this model application are extremely useful in the identification of priority management areas.

#### 4.4.2 GAMES MODEL

The GAMES model (the Guelph model for evaluating the effects of Agricultural Management Systems on Erosion and Sedimentation) was applied to three small watersheds in the Avon River basin and two in the Thames River basin (Figure 5). The objectives of the model applications were to estimate sources and rates of

TABLE 6. Gross Annual Erosion (t), Unit-Area Erosion (t/ha/year) and Unit-Area Erosion by Crop Type and Slope (t/ha/year), Based on Coleman (Draft, 1981).

CATEGORY	AREA (ha)	GROSS EROSION	UNIT-AREA EROSION BY CROP TYPE AND SLOPE					
			0 - 1%	2.5 - 5%	5 - 7%	7 - 10%	10 - 15%	>15%
A. Intensive Agriculture	5509.3	51092.4						
A1. Corn Monoculture	1738.7	19554.3	7.2(1503.5)	27.3(184.8)	45.7 (6.3)	52.9 (4.4)	71.2(37.2)	205.9 (2.5)
A2. Bean Monoculture	591.5	4553.8	7.4 (582.2)	26.4 (9.3)	-	-	-	-
A3. Corn/Bean System	2238.9	19656.7	4.9(1836.8)	20.6(317.2)	28.2(20.3)	43.9(25.5)	56.1(27.5)	76.5(11.6)
A4. Bean/Corn System	586.9	4769.4	5.1 (527.6)	16.1 (20.1)	31.6(20.8)	44.8(11.3)	66.0 (2.3)	91.6 (4.8)
A5. Field Vegetables	353.3	2558.2	6.9 (352.2)	24.2 (0.2)	-	-	-	136.9 (0.9)
B. Medium Intensity Agriculture	5418.4	29727.9						
B1. Mixed Corn/Bean/Small Grain System	4911.8	27111.7	3.4(4199.7)	12.8(526.2)	20.8(51.3)	28.0(52.5)	38.3(60.8)	58.1(21.2)
B2. Grain System	506.6	2616.2	3.6 (449.4)	14.8 (50.4)	22.2 (1.4)	-	41.0 (5.4)	-
C. Low Intensity Agriculture	1437.8	2560.0						
C1. Hay System	1113.8	1469.8	0.7 (922.7)	2.5(123.4)	3.6 (4.7)	5.3 (4.6)	6.3(35.8)	11.0(22.6)
C2. Pasture System	55.6	70.0	0.4 (43.4)	1.6 (1.3)	2.5 (1.5)	4.2 (1.2)	4.3 (6.2)	7.4 (2.1)
C3. Grazing System	257.6	991.9	0.7 (133.1)	2.5 (29.6)	4.2 (5.0)	5.4(15.6)	7.4(31.6)	11.4(42.6)
C4. Wooded Pasture System	10.8	28.3	2.6 (10.8)	-	-	-	-	-
D. Rural Non-Farm Uses	1993.0	309.8						

( ) Area in ha



TABLE 7. Effects of Management Practices on Erosion and Phosphorus Loading, Based on Coleman (Draft, 1981).





MANAGEMENT PRACTICE	AREA in ha	GROSS EROSION (t)	EROSION REDUCTION (t)	LOADING REDUCTION (t)	TOTAL P* REDUCTION (t)	SOL.P** REDUCTION (t)
1. CROSS SLOPE FARMING	16230	83967	7709	1818	0.772	0.147
2. CONTOUR FARMING	16230	83967	15416	3636	1.544	
3. CROSS SLOPE FARMING WITH STRIPES	16230	83967	21129	5462	2.312	0.445
4. STRIP CROPPING ON THE CONTOUR	16230	83967	26702	6877	2.912	0.559
5. CROSS SLOPE FARMING MONOCULTURES	2330	23988	1886	427	0.181	0.340
6. CONTOUR FARMING MONOCULTURES	2330	23988	3718	855	0.362	0.690
7. CROSS SLOPE FARMING WITH STRIPS MONOCULTURES	2330	23988	5051	1225	0.518	0.100
8. STRIP CROPPING ON THE CONTOURS MONOCULTURES	2330	23988	6344	1590	0.673	0.129
9. CROSS SLOPE FARMING INTENSIVE SYSTEMS	5155	48676	4538	981	0.415	0.800
10. CONTOUR FARMING INTENSIVE SYSTEMS	5155	48676	9066	1963	0.830	0.160
11. CROSS SLOPE FARMING WITH STRIPS INTENSIVE SYSTEM	5155	48676	12289	2852	1.208	0.232
12. STRIP CROPPING ON THE CONTOUR INTENSIVE SYSTEMS	5155	48676	15408	3742	1.581	0.304

\* Total P - Total phosphorus

\*\* Sol. P - Soluble phosphorus

# SOIL LOSS IN TONNES PER HECTARE PER YEAR

## LEGEND

-  HIGH MORE THAN 11 TONNES PER  
HECTARE PER YEAR
-  MEDIUM 2-11 TONNES PER HECTARE  
PER YEAR
-  LOW LESS THAN 2 TONNES PER  
HECTARE PER YEAR
-  BUILT-UP

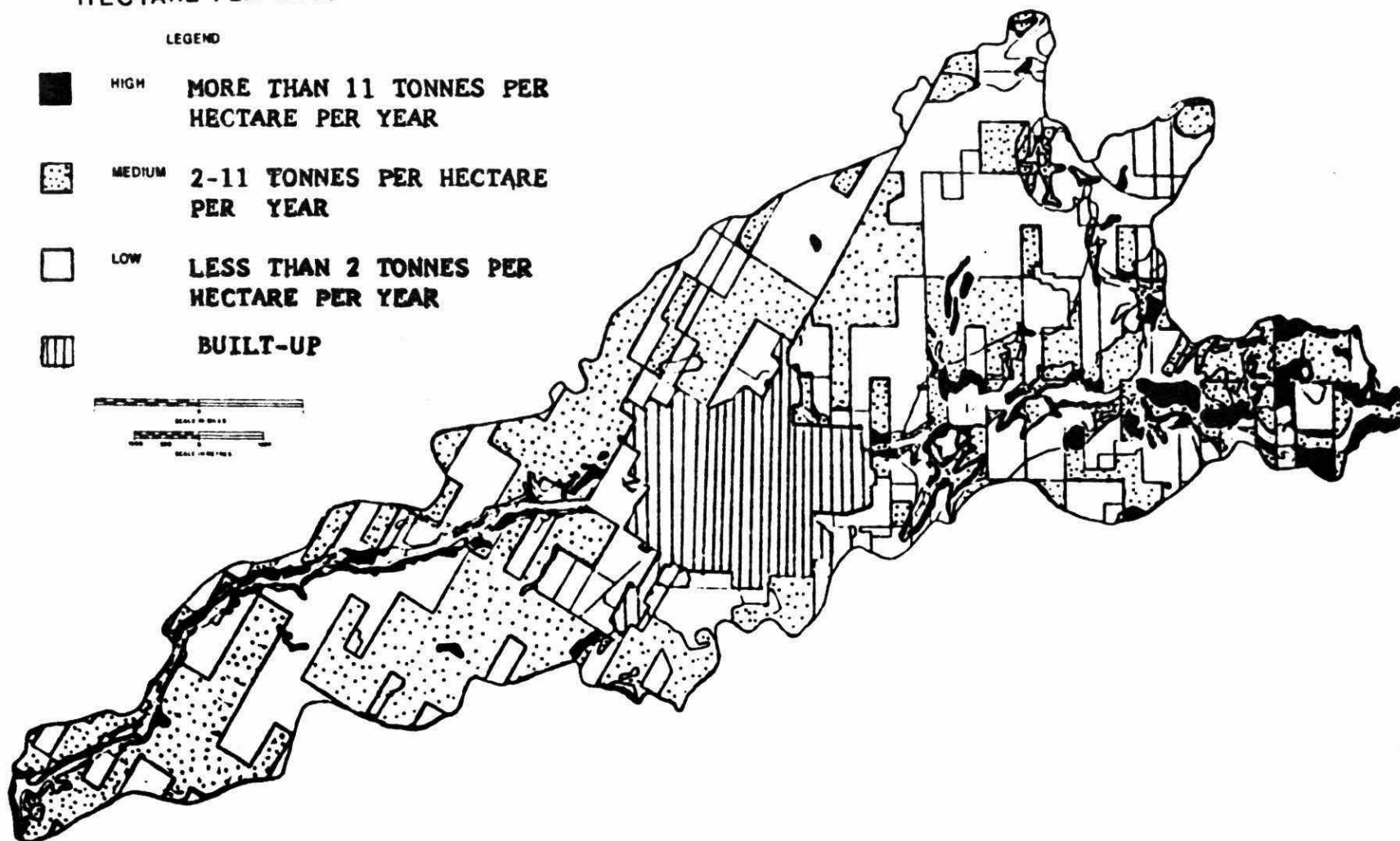
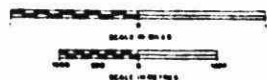


Figure 3. Soil loss distribution per hectare per year in the Avon River basin (Coleman, 1981).

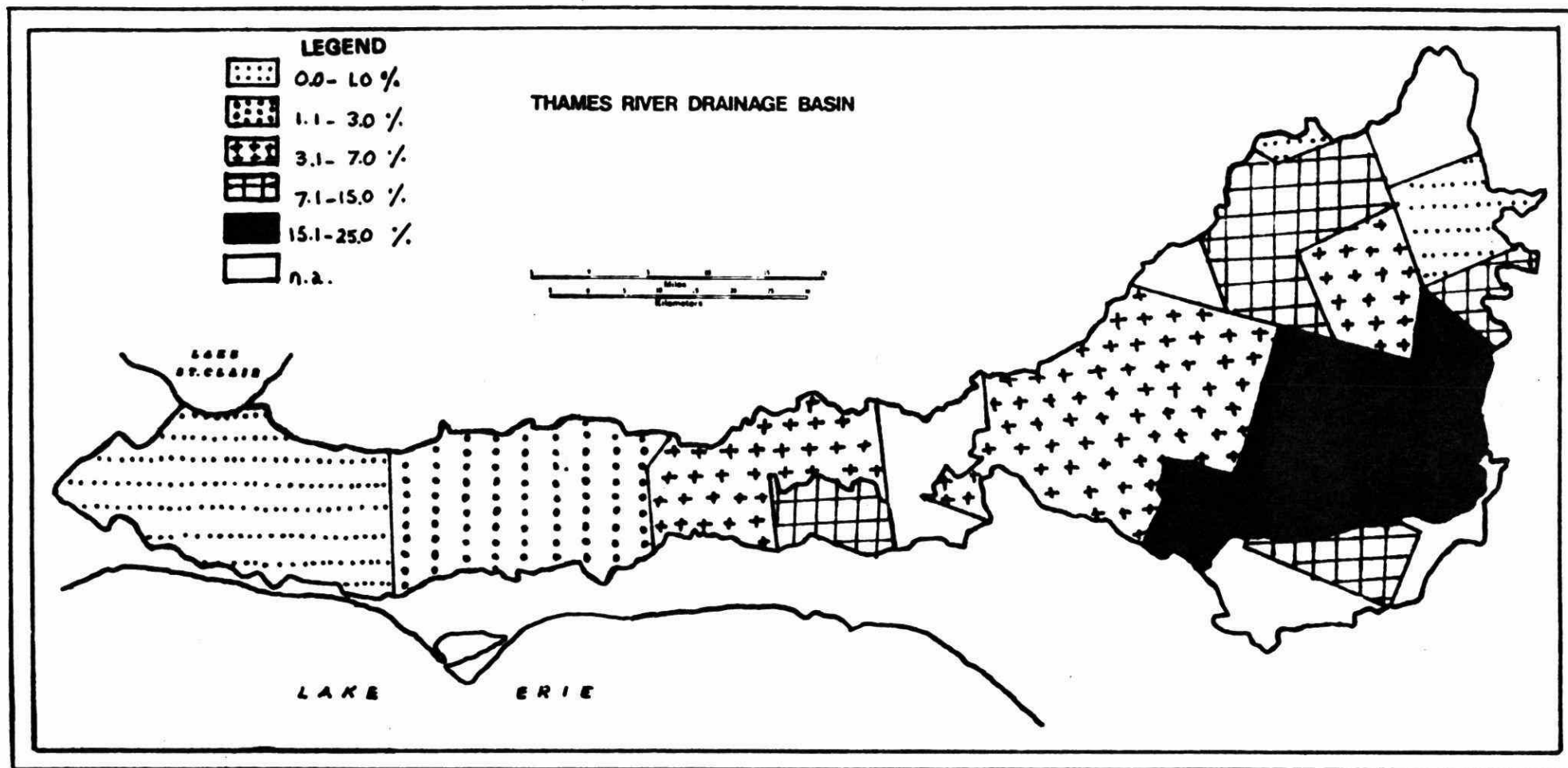


Figure 4. Percentage of rural land with high terrain capability to transport sediment (TRIC, 1982).

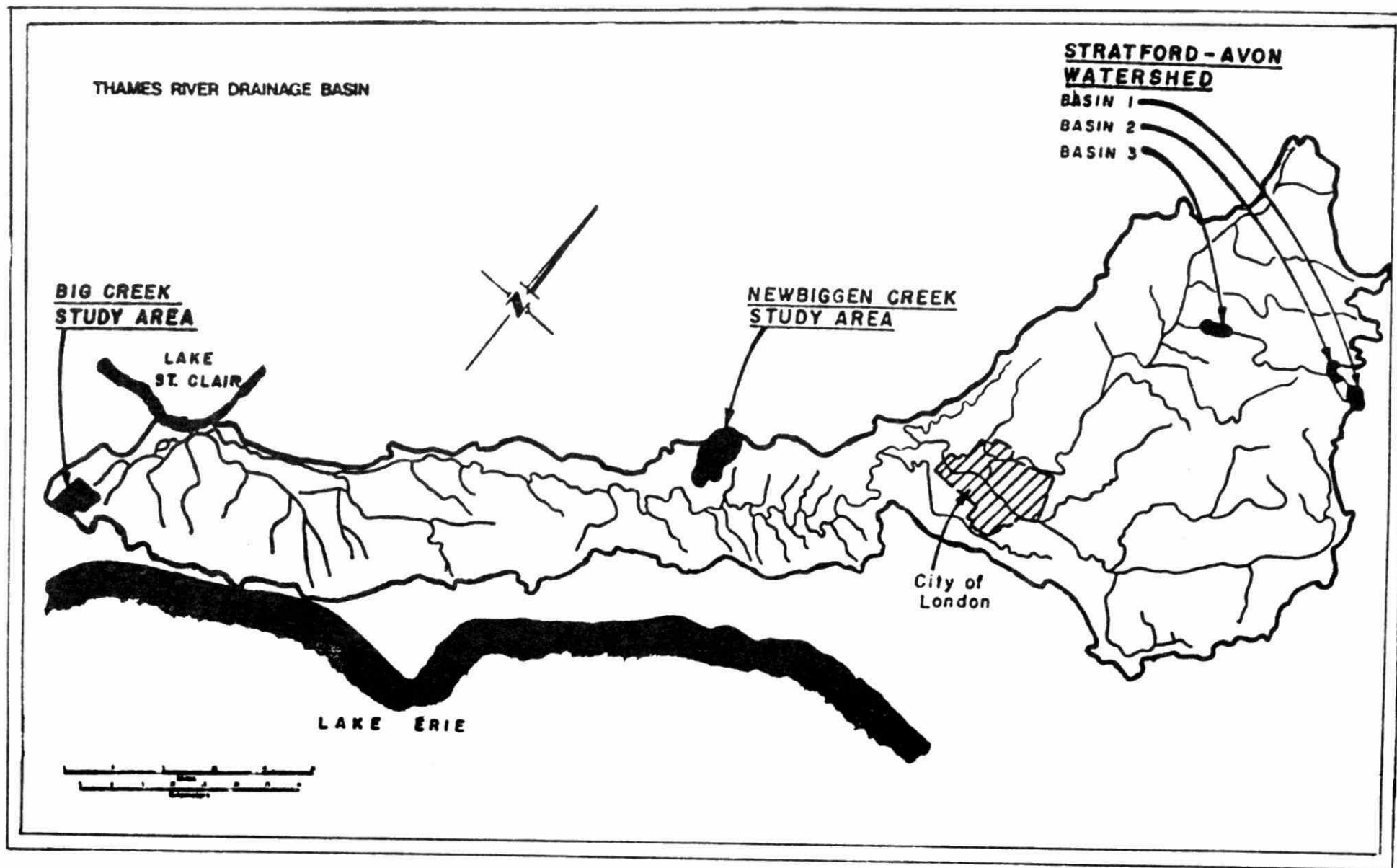


Figure 5. Location of selected watersheds for GAMES model application in the Thames River basin (Dickinson, 1982).

potential soil erosion and fluvial sedimentation in the five selected watersheds and to evaluate the impact of a variety of possible remedial measures.

The soil loss component of GAMES is based on the Universal Soil Loss Equation modified for seasonal considerations. The percentage of the potential field soil loss which can be expected to be delivered to the main stream channel and out of the watershed is determined in GAMES using a special delivery ratio expression. This expression is based on surface roughness, land slope, hydrologic condition (probability of and depth of overland flow), and length of overland flow path (Dickinson, Draft 1982).

The results of the application of GAMES on the three selected small watersheds in the Avon River basin indicate that a major portion of the eroded soil moves within a small percentage of the watershed areas. On the other hand, erosion in the Thames River Study areas is much more uniform across the watersheds. An implication of these observations is that selective control of highly erodible sites in the Avon River watershed could greatly reduce the total erosion. Highly erodible sites do not appear to be present in the Thames River watersheds, and any reduction desired in the overall watershed erosion would require that control measures be applied over most of the watershed areas.

Dickinson (Draft, 1982) confirmed that relatively steeply-sloped, fallow fields near main stream channels exhibit both high erosion rates and high sediment yields. Relatively level fields located near the stream and having poor or imperfect internal drainage have high delivery ratios and tend to yield moderate to high sediment loads. Steeply-sloped, row-cropped fields remote from good drainage channels may exhibit serious local erosion but contribute little or no sediment to the stream. The impact of alternative crop and soil management practices on potential soil loss and sediment

delivered in the Avon demonstration watershed is given in Table 8 and the location of site-specific remedial measures are given in Figure 6.

#### 4.4.3 ANSWERS Model

ANSWERS is a distributed watershed model which simulates the flow of water and sediment from various elements of the watershed during and immediately following a rainfall event (Beasley and Huggins, 1980). The model is designed to be used as a tool for the planning and evaluation of strategies to control agricultural NPS pollution.

Preliminary results from ANSWERS applications to the Avon River basin indicate that areas with a high erosion are concentrated in the more rolling southeast section of the basin and in the southwest where finer soils and more intensive farming practices are found. Again, a strong relationship between high erosion rate and the type of crop was observed (Figure 7). Notably, those elements in the watershed identified as either a corn or bean monoculture exhibited high erosion rates (Senyshyn, Draft, 1982).

The experience with ANSWERS on the Avon River watershed suggests that the model requires a large amount of data for a successful calibration and verification which may reduce its usefulness for planning purposes.

### 5. AGRICULTURAL NPS CONTROL OPTIONS

Control of NPS pollution from agricultural land is a difficult problem and it poses an important public challenge. Because the technological and economical limitations can be greater when controlling agricultural NPS than when controlling point sources, it is essential for a successful outcome to launch a joint program with participation by individual land users, farming organizations, academia, consulting firms as well as local, provincial and federal governments.

TABLE 8. Impact of Alternative Crop and Soil Management Practices on Potential Soil Loss and Sediment Delivered in the Stratford/Avon Demonstration Watershed (After Dickinson, Draft, 1982).

Crop and Soil Management Practices	Potential Soil Loss (tonnes)	Sediment Delivered (tonnes)	Reduction in	
			Potential Soil Loss (%)	Sediment Delivered (%)
<u>Spring Conditions</u>				
1. No residue over winter, fall ploughed	1600	410	Basic Reference Levels	
2. Cross-slope farming ('81-'82 conditions) - 35% of area	1345	305	16 <sup>1</sup>	26 <sup>1</sup>
3. Cross-slope farming + grassed waterways on 1% of area	1345	285	16	30
4. Cross-slope farming, grassed waterways, + strip-cropping at (1)* - 2% of area	1280	275	20	33
5. Cross-slope farming, grassed waterways, + strip-cropping at (1) and (2) - 5% of area	1275	275	20	33
6. Cross-slope farming, grassed waterways, + strip-cropping at (1), (2) and (3) - 6% of area	1235	245	23	40
7. Cross-slope farming, grassed waterways, + strip-cropping at (1),(2),(3), and (4) - 8% of area	1185	200	'81-'82 Reference Levels 26	51
8. Cross-slope farming, fall moldboard ploughing (on total basin).	1180	295	26 <sup>2</sup>	28 <sup>2</sup>
9. Crop rotations, fall moldboard ploughing (on total basin)	850	210	47	49

TABLE 8 - (Con't)

Crop and Soil Management Practices	Potential Soil Loss (tonnes)	Sediment Delivered (tonnes)	Reduction in	
			Potential Soil Loss (%)	Sediment Delivered (%)
10.No residue over winter, spring moldboard ploughing	1100	275	31	33
12.Residue left over winter, spring moldboard ploughing (on total basin)	850	135	47(28)	67(33)
13.No residue over winter, conservation tillage	435	100	73	76
14.Residue left over winter, conservation tillage	350	50	78	88
<u>Summer Condition</u>				
1. No conservation measures	1695	5		
2. '81-'82 conservation strategies	1635	10		

1 - Reduction expressed as a percentage of the basic reference level.

2 - Reduction expressed as a percentage of the '81-'82 reference level.

\* - Numbers in brackets refer to demonstration areas shown on Figure 6.



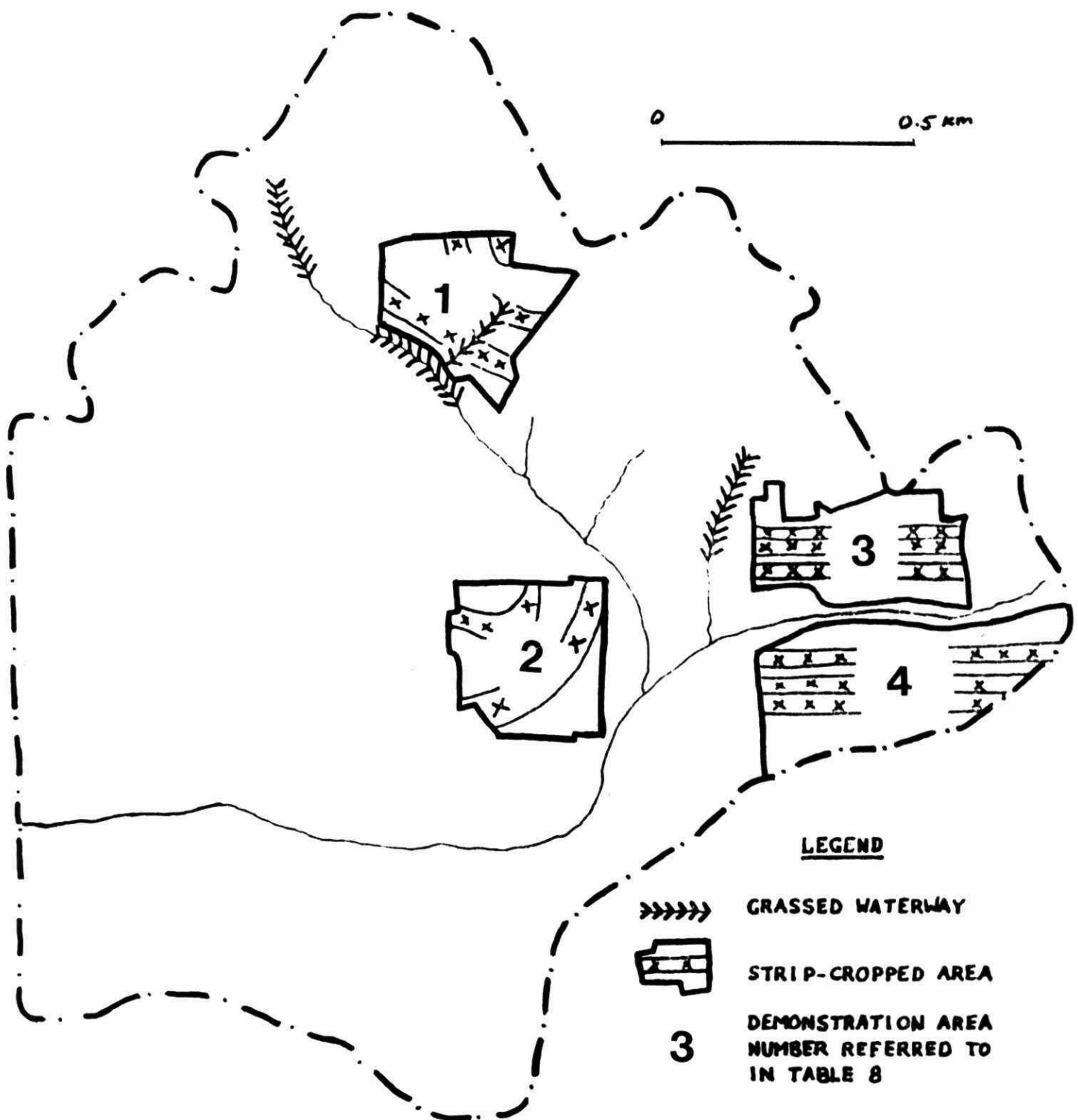
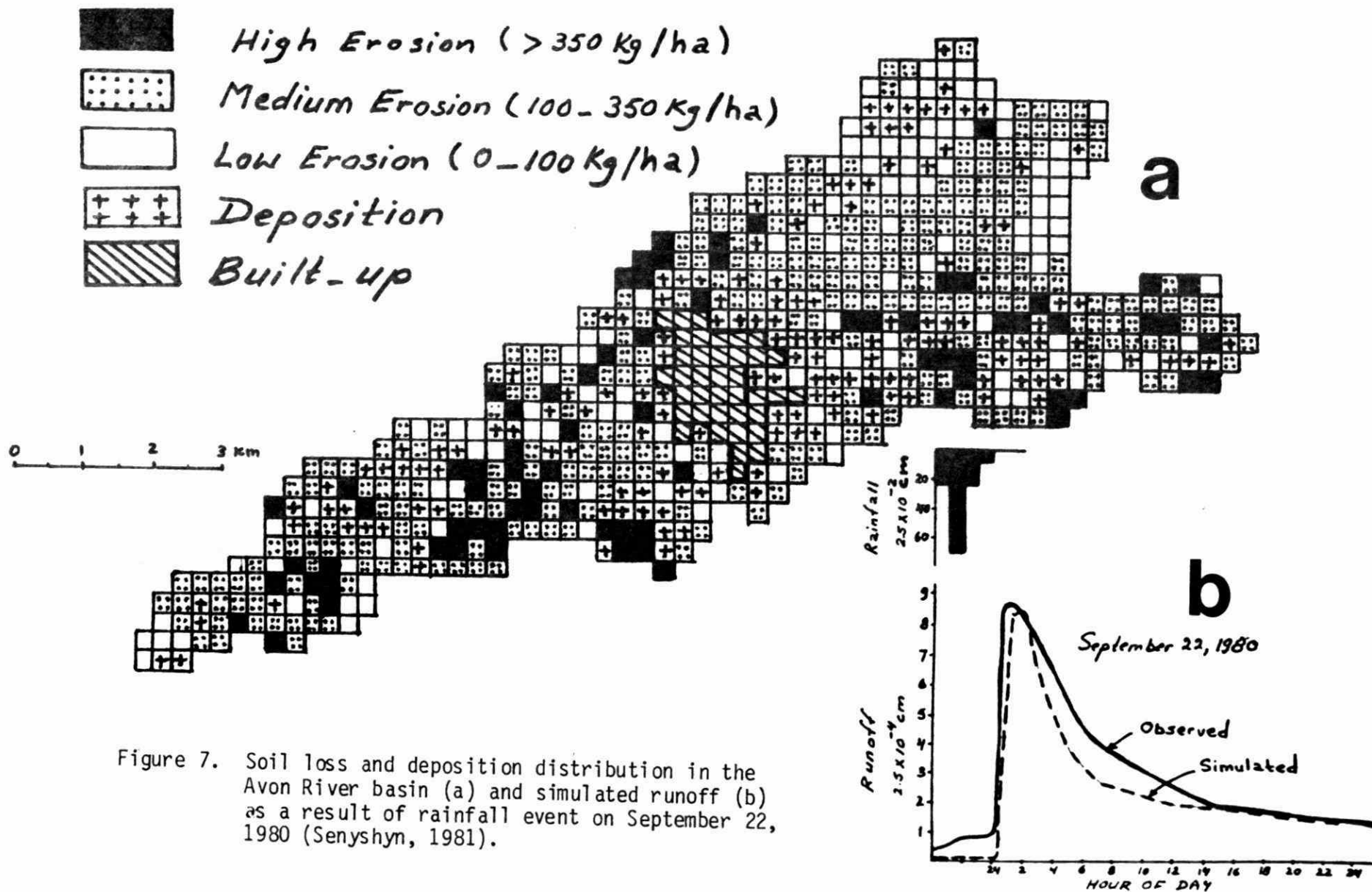


Figure 6. Location of site-specific remedial measures considered in the Stratford/Avon demonstration watershed (Dickinson, 1982).



At present, the emphasis for the control of agricultural NPS is being placed upon the use of the concept of best management practices. This concept is based on the assumption that the environmental objectives and sound agricultural practices are consistent, and that acceptable environmental standards can be met in a manner which is practical and reasonably economical for the farmer.

### 5.1 Criteria For Viable Control Options

For control measures to be successful, a number of selection criteria have to be met. First, the controls must meet the test of being practical within the context of agricultural operations. This implies that water quality management cannot be addressed independently, but only in the context of an overall crop, soil and water management program. Secondly, the control measures must be economical and cost-effective. The farmer expects and deserves a reasonable economic return on his investment. Control measures that put the farmer out of business are self-defeating. Thirdly, the control measures must be site-specific. Agricultural pollution can best be controlled by measures adapted to existing conditions on a given farm rather than by uniform requirements.

### 5.2 Control Measures

At present, considerable literature is available on remedial measures to control NPS pollution, in general, and agricultural NPS, in particular. Extensive information already exists on the applicability, advantages and disadvantages of these measures. Today, we can with confidence identify major pollution problems attributed to agricultural sources and select measures which can significantly reduce the pollutants causing these problems (Switzer-Howse, 1982).

We have learned that measures such as conservation tillage, increased use of surface residues, crop rotations, winter cover crops, strip cropping, contour cropping, grassed waterways,

terraces, runoff diversions, buffer strips, sediment traps, improved drainage outlets through environmentally sound construction practices and removal of land from intensive cultivation are proven measures to reduce erosion.

Regulating nutrient supply to meet crop requirements, incorporating fertilizer into soil, crop rotations, winter cover crops, proper timing and erosion controls are effective measures to reduce nutrient losses.

Livestock management practices include proper manure containment and storage facilities, exclusion of cattle access to streams with alternate watering facilities, and disposal of manure on sites with low erosion potential and away from watercourses.

Pesticide management practices include elimination of excess use, modifications of timing and application procedures, and elimination of spills through proper handling procedures (Switzer-Howse, 1982).

### 5.3 Implementation Strategies

#### 5.3.1 Emphasis on Erosion Control

Sufficient investigation has been conducted, under a variety of conditions in Ontario, to document the fact that erosion is a threat to the quality of our water resources. There is also a strong reason to believe that the erosion process has been accelerating in Ontario during the past 20 years. Technological advances such as new high-powered machinery, improved crop varieties, new fertilizers and pesticides, and extensive drainage networks made it possible to work larger areas and to obtain higher yields than ever before. Large multirow equipment and field consolidation programs led to removal of fence rows and natural barriers; to creation of long erosion-prone slopes; to excessive tillage without regard to slope direction; and to growing of crops on lands that were once considered uneconomical to farm. Increased value of corn, soybeans and white beans encouraged farmers to switch to these crops at the expense of

grass and legumes. Often these crops are grown continuously, thus greatly reducing and sometimes eliminating crop rotations. All this has led to an increase in soil erosion and to signs of yield drop in areas which erode at levels much higher than soil regeneration rates (over 11 t/ha/year).

The extensive surface drainage networks on agricultural lands have also contributed to higher erosion levels due to poor design and poor construction and maintenance; to increased sedimentation problems due to clogging of stream channels, silting of ponds and reservoirs; and to escalation in maintenance costs.

Based on the above, it is reasonable to conclude that erosion controls play a key role or, possibly, the dominant role in agricultural NPS control. In recognition of the magnitude and severity of the soil erosion problem, the Ontario Chapter of the Soil Conservation Society of America has recently issued a discussion paper on soil erosion (SCSA - Ontario Chapter, 1982). The paper suggested that the provincial government should respond immediately to the International Joint Commission report regarding the PLUARG studies, acknowledge the severity of the soil erosion problem in Ontario and commit itself to remedial action.

#### 5.3.2 Emphasis on Priority Areas

In times of scarce resources and economic constraints, the initial emphasis of an agricultural NPS control program should be targetted towards areas with the most severe erosion problems and/or high sediment delivery capability. Available evidence indicates that areas with relatively steep slopes, fine-textured soils, high percentage of continuous row crops, and extensive drainage networks are eroding at levels higher than 11 t/ha/ year. There is little doubt that, without preventive measures, these areas will ultimately deplete their top soil layers along with their agricultural capabilities. When nutrient-laden sediment is transported from these areas to receiving streams it causes

channel siltation and water quality impairment. Therefore, it is logical to concentrate initial efforts and resources on these obvious critical areas. In doing so, the return on investment will be most cost-effective.

### 5.3.3 Emphasis on Other Supportive Programs

For a set of agricultural NPS control measures that are practical, cost-effective and site-specific to be implemented successfully the following programs have to be met:

#### A. Technical Assistance Program:

The farmer must be provided with specialized technical assistance which may include advice, engineering design for structural work, supervision, and instructions in new agricultural practices.

#### B. Economic Incentive Program:

The farmer may require some economic incentive. The concept of cost-sharing and provisions of reasonable subsidies for remedial measures may be essential for a successful agricultural NPS program especially in the initial phase. Where water quality concerns exist with no substantial agricultural production problems, financial assistance will be necessary.

#### C. Information and Education Program:

Information packages which provide fact sheets on agricultural NPS control measures and emphasize water quality goals as well as farm productivity goals must be disseminated to farmers. Meetings and presentations to farm groups; displays and exhibits at agricultural fairs; development, printing and distribution of practical guides on NPS controls; demonstration projects; and press and media coverage are all important elements of a public education program which emphasizes the rural environmental concerns.

While soil erosion is one of the most important problems facing agriculture in Ontario today, and requires substantial investment in order to solve, there are a number of cultural, non-structural measures that are extremely effective in improving water quality, yet practically cost-free. For example, elimination of excessive use of fertilizers and pesticides; incorporation of these chemicals into the soils where possible; modification of timing and application procedures, or reduction in spills of pesticides through better handling procedures are all measures that are in the interest of the farmer as well as the environment. Educational programs are the vehicles to promote these ideas.

D. Research Program:

Research continues to be critical to refine existing knowledge on agricultural NPS pollution and control. The objective of research should be to develop sensible, economical and efficient strategies for managing agricultural pollution. Monitoring is also important in order to measure the effects of control and to review and revise agricultural practices as new information becomes available. The following is the authors' suggested list of research needs in the field of agricultural NPS pollution and control:

- a) A better basis for defining soil erosion tolerances in terms of crop production and water quality objectives.
- b) A better understanding of the instream phosphorus pathways.
- c) A better predictive capability to quantify the reduction of pollutant loads or water quality benefits as a result of implementation of agricultural NPS controls.



- d) Development of simple methods to identify problem areas in terms of erosion and/or sediment delivery.
- e) Testing and refinements of existing agricultural NPS models to determine the optimal mix of control measures and to evaluate cost-effectiveness, impacts on crop yield and risks of failure.
- f) Documentation of good and bad farming practices in Ontario in terms of crop production and water quality.
- g) Research on alternative schemes for financing agricultural NPS controls.
- h) Research on the adequacy of existing environmental laws.

## 6. CONCLUSIONS

Research in Ontario has established that agriculture contributes large amounts of sediment, nutrients, pesticides and bacteria to receiving waters. Several techniques and models have been developed and/or applied in Ontario to address the definition and quantification of agricultural NPS pollution and to evaluate proposed remedial measures. The results of the application of these techniques and models have been promising. Further testing and refinement of existing agricultural NPS models, however, are necessary to determine the optimal mix of control measures and to evaluate cost-effectiveness, impacts on crop yield and risks of failure.

Control of nonpoint source pollution from agricultural land is a difficult problem and it poses an important public challenge. For control measures to be successful they must meet the test of being practical, economical, cost-effective and site-specific. The implementation strategy for agricultural control measures should emphasize erosion control, priority areas and supportive programs which include a combination of technical assistance to farmers, economic incentives, education and research.



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EVALUATION OF THE PERFORMANCE OF  
A COMBINED SEWER OVERFLOW RETENTION TANK

BY

W. M. WONG AND G. ZUKOVS

WASTEWATER TREATMENT SECTION

LABORATORY SERVICES AND APPLIED RESEARCH BRANCH

ONTARIO MINISTRY OF THE ENVIRONMENT

SUMMARY

The performance of the combined sewer overflow tank near Hyde Avenue in the Borough of York was studied in the summer months (June to October) of 1977 and 1978. The entire study period spanned 276 days during which time 50 storms occurred. Thirty-three storm events produced inflow to the tank. Seventeen of these events were wholly retained within the tank with the remainder resulting in a total of  $0.47 \times 10^6 \text{ m}^3$  of overflow to Black Creek.

The presence of the tank reduced overflow volume by 18%. Pollutant loadings for BOD, solids and nutrients were reduced by an average of 38%-47% of the influent loading including wholly retained events and events with overflow. The tank was, therefore, an effective device for reducing pollution from combined sewer overflow.

The outlet barrier of the tank removed practically all floating substances from the overflow to the creek, greatly enhancing the aesthetic quality of the overflow.

## INTRODUCTION

A joint study was carried out by the Ontario Ministry of Environment and the Borough of York in Metropolitan Toronto to assess the performance of the combined sewer overflow (CSO) detention tank near Black Creek in the summer months (June to October) of 1977 and 1978. The tank intercepts the flows from the tributary combined sewer system when the flowrate in the sewer system exceeds a predetermined limit. The tank retains that fraction of the intercepted flow not exceeding its own capacity and overflows the remaining fraction to Black Creek after sedimentation. The flow retained by the tank is returned to the sewer system after the storm event. This report presents the findings of the study.

## OBJECTIVE

The study objective was to evaluate the performance of the CSO tank through a monitoring program. The tank performance was defined as the effectiveness in reducing the frequency, volume and pollutant loading of combined sewer overflows to Black Creek.

## BACKGROUND

### General

The catchment area, shown in Figure 1, is a relatively older section of Metropolitan Toronto. It has an area of 834 ha and an estimated population of 70,000. Although fully developed some time ago, redevelopment had commenced in the late sixties to meet the needs of the increasing population brought by social and economic growth.

Nearly the whole catchment area was and still is serviced by a combined sewer system. The combined sewer system discharges into the Metro Toronto Trunk Sewer (MTTS), which is tributary to the Humber Water Pollution Control Plant (WPCP). Before the combined sewer overflow tank was built, all excess combined sewage overflowed into Black Creek without treatment.

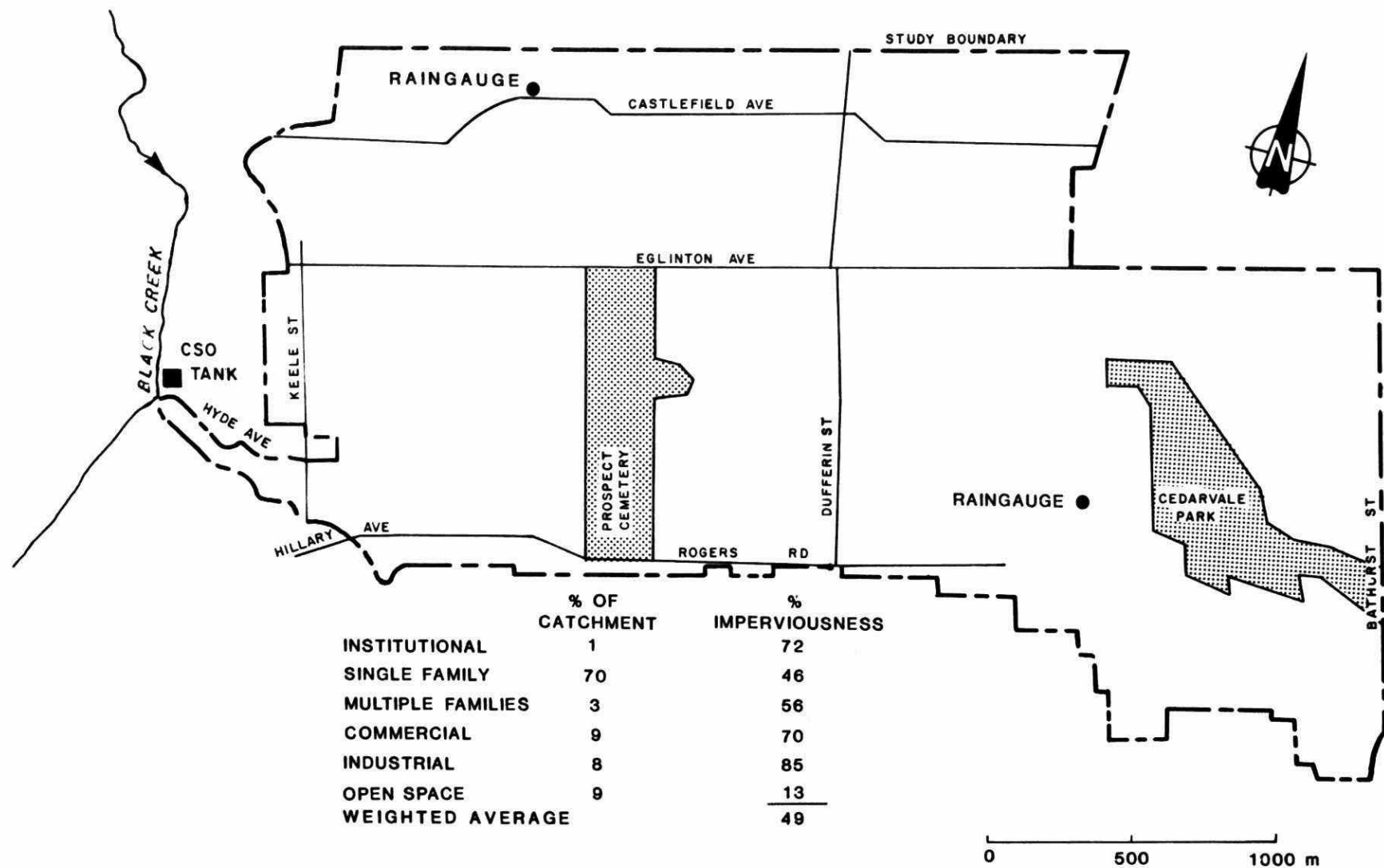


FIGURE 1: CATCHMENT TRIBUTARY TO HYDE AVE CSO TANK



One option for the Borough to deal with the additional combined sewage generated by the urban redevelopment was to take on a sewer separation program. This option was expensive and would take many years to complete. Another option, partial separation of the combined sewers, was rejected as it would not significantly reduce overflows. In 1968, it was decided that rezoning and redevelopment could be continued only if the combined sewer overflows to Black Creek were chlorinated and detained in a holding tank before being discharged. The CSO tank was constructed and placed in operation in 1972.

#### Catchment And Sewer System Characteristics

The study area is bounded by Keele Street to the west, Castlefield Avenue to the north, Bathurst Street to the east and Rogers Road to the south (see Figure 1). The topography of the catchment area is generally flat with a gradual decline westerly towards Black Creek.

Six major land uses can be identified in the catchment area. The residential areas are mostly older homes with roof leaders generally discharging to the ground surface. Lots have a small frontage with sidewalks directly adjacent to the roads. Institutions are primarily schools which have most of their playgrounds paved. The main industrial area is along Castlefield Avenue, west of Dufferin Street. The major open space areas are Cedarvale Park and Prospect Cemetery. The main commercial area is along Eglinton Avenue West, with a secondary area along Dufferin Street north of Eglinton Avenue West.

The area weighted percent imperviousness of the whole catchment was estimated to be 49%.

The sewer system is shown in Figure 2. The Keele Street trunk sewer serves Area 1 and the Hillary Avenue trunk sewer serves Area 2. The sewers join together at the intersection of Keele Street and Hillary Avenue and discharge into the Metro Toronto Trunk Sewer (MTTS).

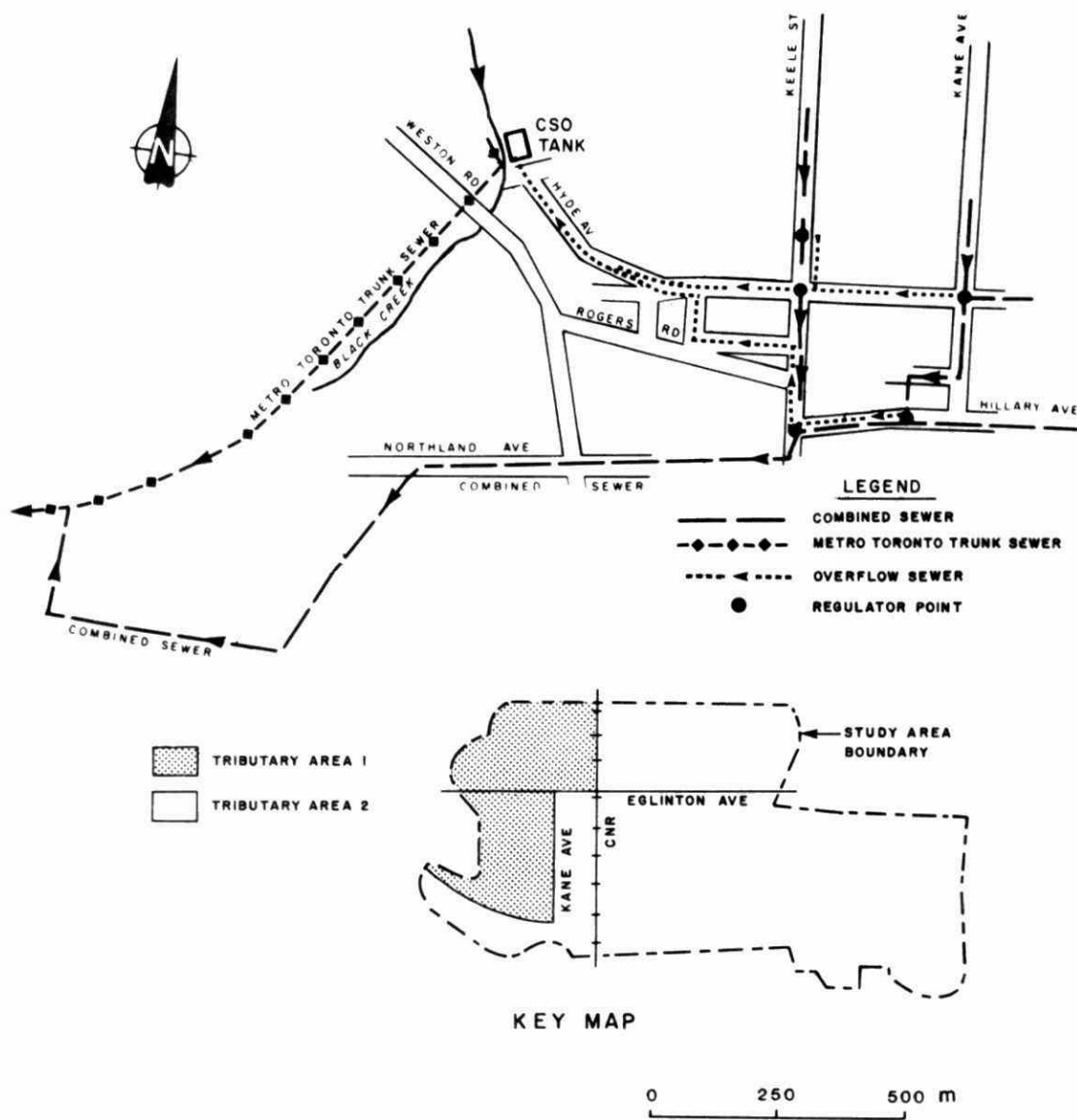


FIGURE 2: TANK LOCATION AND TRIBUTARY SEWERS

During wet weather, the operation of the system is complex. There are six possible overflow locations as shown in Figure 3. All overflows, except those occurring at Regulator No. 1, are collected by the overflow sewers and discharged to the tank. Regulator No. 1 discharges directly to Black Creek.

#### CSO Tank Characteristics And Operation

The CSO tank, illustrated in Figure 4, has dimensions of 54.2mx38.1mx4.3m. It is constructed underground and covered with a roof forming part of a grassed park area. A chlorination chamber is located at the inlet end of the tank.

The storage capacity of the tank to the overflow depth (3.5 m) is 7,400 m<sup>3</sup>. This capacity is equal to 0.9 mm of storage over the 834 ha catchment area.

The tank was sized to provide 10 minutes detention after chlorination, at an average flowrate of 14,150 L/s, half the maximum design hydraulic flowrate of the inlet sewers. At the time of the study, chlorination of the influent was no longer practised and the tank served as an overflow detention tank. The present study evaluated this latter function.

Drainage of the tank to the MTTs is controlled by a hydraulic sluice gate which is open during dry weather to drain infiltration flows; it automatically closes during storms when the water level in the tank reaches a predetermined level. After a storm event, Borough personnel open the gate and drain the tank contents back to the MTTs. Emptying of the full tank takes about 11 hours.

The overflow end of the tank has a scum baffle which prevents floatable debris in the sewage from reaching Black Creek.

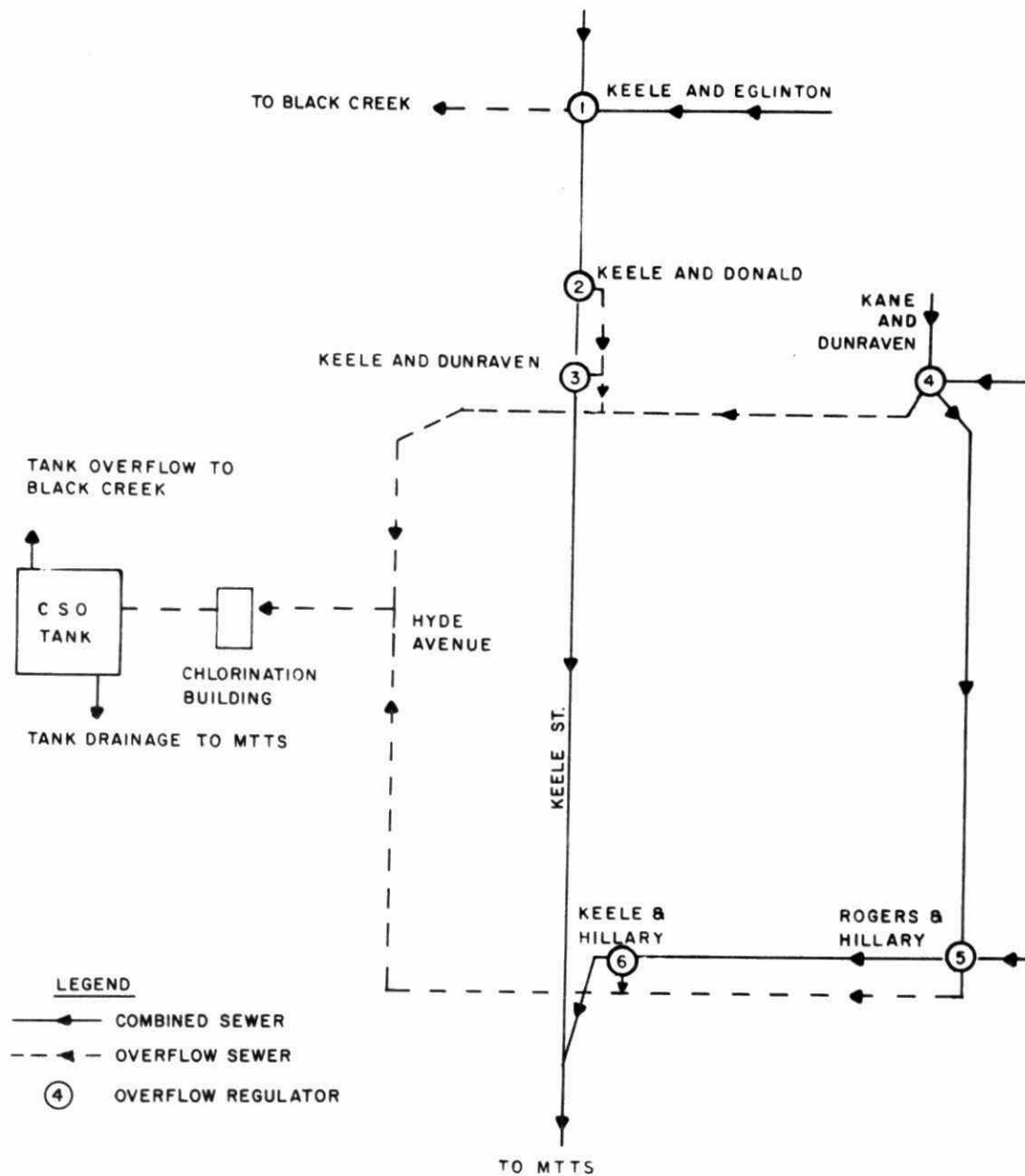
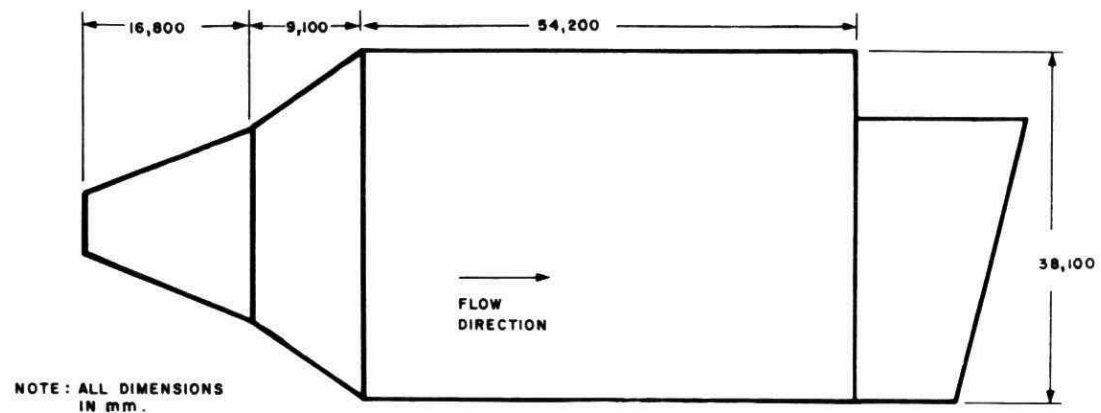


FIGURE 3: DIAGRAM OF FLOW REGULATING SYSTEM



PLAN

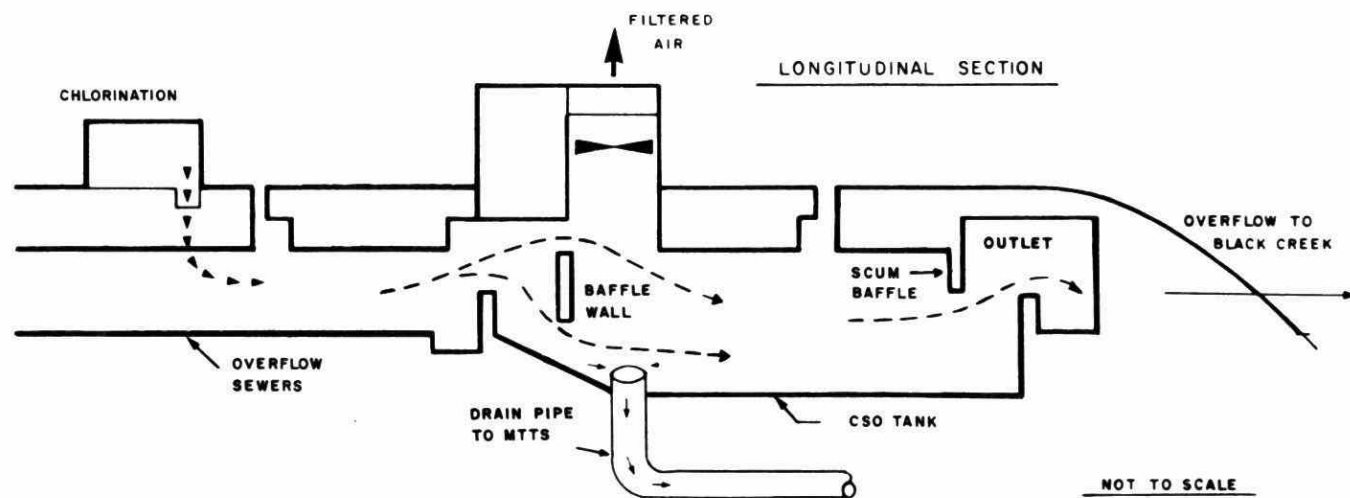


FIGURE 4: CSO TANK DETAILS

## MEASUREMENT TECHNIQUES AND INSTRUMENTATION

### Rainfall Measurements

The prevailing direction of summer storms in the Borough of York is from the west. Accordingly, two raingauges were used, one in the northwest part and the other in the southeast part of the catchment area (see Figure 1). They were of the tipping bucket type, recording on 24-hour charts with a time resolution of approximately 2.5 minutes.

### Dry Weather Sewer System Measurements

In order to obtain total dry weather flow, measurements were made at separate locations in the Hillary Avenue and the Keele Street trunk sewers.

Manning's equation was used to determine flowrates. The value of Minnings "n" was first determined by in-sewer measurements.

Flow depths were measured with portable level recorders mounted in manholes. The Hillary Avenue trunk sewer was monitored from September 29 to October 12, 1978, and the Keele Street trunk sewer from September 6 to September 11, 1978. Sewer slopes were determined by survey.

The quality of the dry weather flow was determined from composite samples analyzed for chemical parameters, and grab samples analyzed for bacteriological parameters. It was assumed that the quality of the sewage in the Hillary Avenue and Keele Street sewers was essentially identical, thus sampling activity was concentrated on the more accessible Hillary Avenue trunk sewer.

Sampling was carried out between September 30 and October 14, 1977. Parameters analyzed were: BOD<sub>5</sub>, COD, TSS, VSS, NH<sub>3</sub>-N, NO<sub>3</sub>-N, TKN, TP and Alkalinity as CaCO<sub>3</sub>.

Sampling was carried out for bacteriological quality during the 1977 period of investigation. Samples were analyzed for fecal coliform, total coliforms and enterococcus bacteria.

#### CSO Tank System Measurements

Monitoring commenced in June, 1977 and continued until August, 1978. The tank level was measured with a level recorder. The retained volume was calculated from the measured level employing a stage-volume relationship determined from engineering drawings of the tank.

The overflow rate from the CSO tank was calculated from the head on the tank effluent weir which was measured by means of a bubbler level recorder. Flows were compared according to the broadcrested weir formula:

$$Q = CLH^{3/2}$$

where Q = flow in L/s

C = coefficient of discharge for broadcrested weir (5)

(=  $4.83 \times 10^{-5}$ ,  $5.69 \times 10^{-5}$ ,  $6.12 \times 10^{-5}$ ,  
respectively for H=150, 300 and 450 mm)

L = length of the weir crest in mm

(= 35,000 and 25,800 mm, respectively  
for H>600 mm and H<600 mm)

H = head of water on weir in mm

Samples needed for characterizing the inflow and the overflow of the CSO tank were collected with automatic samplers. in the period from July to September, 1977. Bacteriological samples were manually taken, if staff were present during precipitation events.

## Data Reduction

### Defining Event Characteristics

All data collected for storm events with inflows to the CSO tank were arranged in a chronological order. In a day with two storms, if the flow from the second storm reached the tank before the tank contents were emptied, then the complete data were listed as one event; if the retained flow from the first storm in the tank was emptied before the start of the second storm, the two storms were listed as separate events.

The tank inflow duration was obtained from the tank level recorder chart. Inaccuracy occurred during the initial period of the event because some wet weather flow was lost through the 300 mm under-drain before the tank level rose sufficiently to close the drain gate automatically. The error was unknown but was assumed to be minimal for storms which filled the tank. The instant at which inflow ceased was assumed to occur either when the tank level recorder began to register a constant level or when the overflow rate started to decline, at what appeared to be the natural rate without inflow. The duration taken to fill the tank was taken as the inflow time for the tank level to reach 3,500 mm.

### Method For Wet Weather Flow Computation

The flow from the entire catchment in an event was the sum of (i) flows going into the MTTS and (ii) flows going into the tank (which included the flow retained by the tank and the overflow, if any). Although tank inflow was readily determined from monitored data, there was no measurement of flow in the combined sewers, such that either the flow going to the MTTS or the flow from the entire catchment could be directly determined. The values of these latter two parameters were computed from a synthesized hydrograph similar to the one in Figure 5.



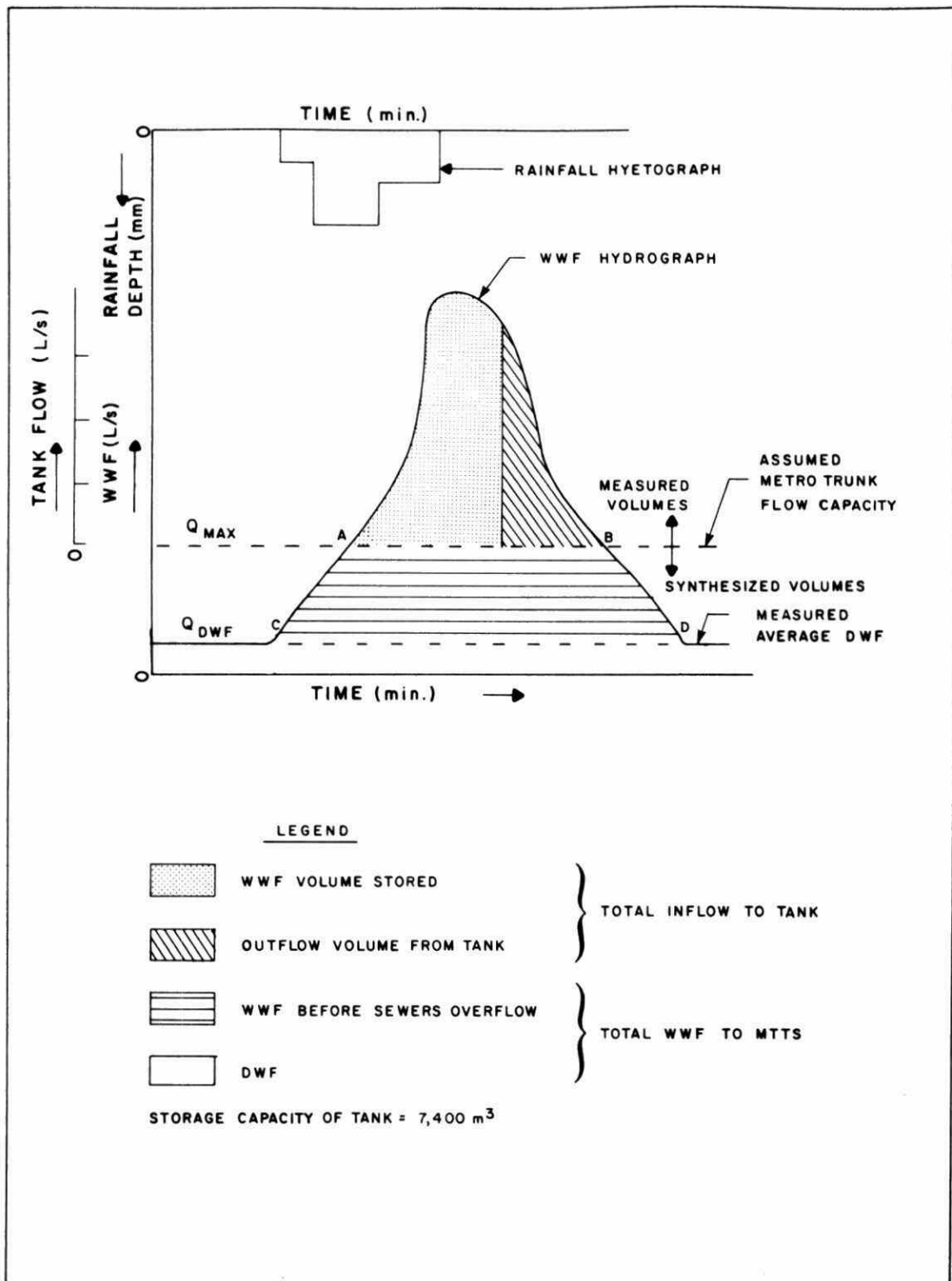


FIGURE 5: WET WEATHER FLOW HYDROGRAPH

The hydrograph synthesis made use of the fact that the flow going to the MTTTS was the sum of the flows in the two trunk sewers (the Keele Street sewer and the Hillary Avenue sewer). See Figure 6. In wet weather, the flow to the MTTTS from these two trunk sewers was determined by the sum of the maximum flows allowed to pass through the most downstream regulator at each of these sewers, i.e. regulators No. 3 and No. 6. By computation, the maximum flows allowed by these two regulators were 1,112 L/s and 3,294 L/s, giving a total of 4,406 L/s.

It was assumed for the sake of analysis that the maximum flow,  $Q_{\max}$ , that would go to the MTTTS was 4,406 L/s and that any flow in excess of  $Q_{\max}$  would be diverted to the tank.

The assumption involves two possible sources of error. First, the two regulators might not start to overflow simultaneously, so some combined sewage might have been discharged to the tank before  $Q_{\max}$  was reached. Secondly, after  $Q_{\max}$  was reached, the increase in head at the regulators would cause some flow in excess of  $Q_{\max}$  to go to the MTTTS. However, due to the complexity of the sewer system and the difficulty of measuring flows at overflow locations, the assumption was made.

When constructing the hydrograph, the portion above the line AB was drawn first from monitored data. Point A, the start of inflow to the tank, was determined from the time at which water level in the tank began to rise. The inflow rate was determined in two ways depending on the situation. If the tank was not filled to capacity, the inflow rate was equal to the rate of increase in volume stored with respect to time. If the tank was overflowing, the tank inflow rate was taken to be equal to the tank overflow rate. The flowrate from the entire catchment at any given time was equal to the sum of  $Q_{\max}$  and the tank inflow rate. This flowrate was plotted against the corresponding time to produce the hydrograph. Point B represents the end of inflow.

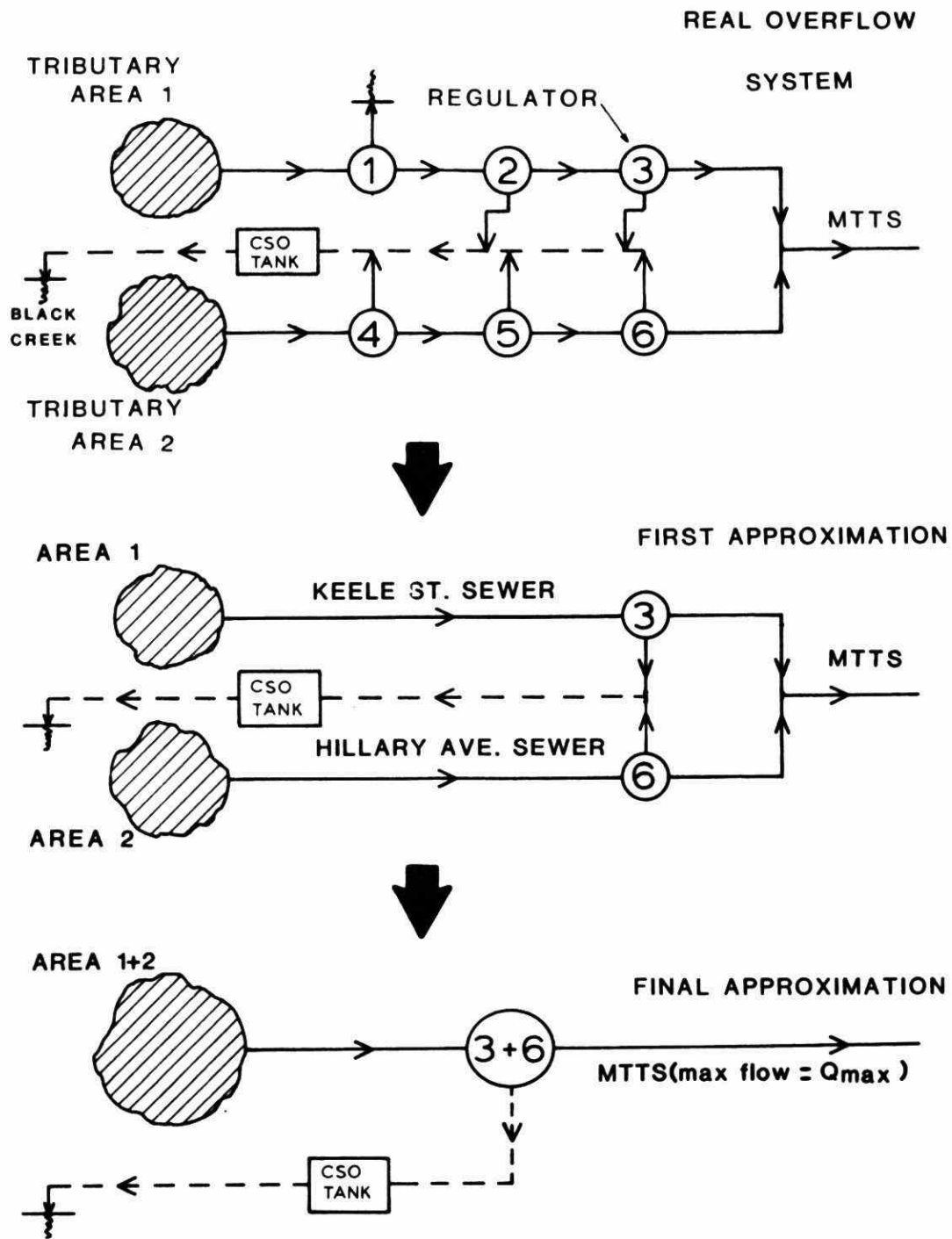


FIGURE 6: APPROXIMATION FOR  $Q_{max}$

Then by projecting the two arms of the hydrograph downwards from points A and B at the same gradients at these two points respectively, points C and D were obtained when the arms met the base flow line. The base flow was the monitored dry weather flow. Points C and D represent the beginning and the end of the storm event.

In theory, the equating of the inflow rate to the overflow rate in the overflow period somewhat distorted the hydrograph because of the storage effect. In the early part of the overflow period, inflow rate was under-estimated and in the latter part of the period, the inflow rate was over-estimated. As a result, the storage effect affected the gradient extrapolated from point B to point D (see Figure 5), and so increased the area of ABDC in Figure 5. The error was unknown but was assumed to be negligible as the total inflow volume must be comparatively large to cause overflow from the tank.

## RESULTS AND DISCUSSION

### Dry Weather Flow Quantity And Quality

The sum of average dry weather flow of the Hillary Avenue and Keele Street trunk sewers, calculated from measured flow depths, was 360 L/s. For a population of 70,000, this flow value yields a DWF contribution of 444 L/capita/day. Although this per capita contribution is a bit low compared to the Metro Toronto average (632 L/capita/day), it seems to be reasonable. The measured 360 L/s is about 8% lower than the design dry weather flow of 390 L/s.

Table 1 shows the dry weather flow quality results. They indicate a dry weather flow quality typical for residential areas.

TABLE 1

AVERAGE DWF QUALITY RESULTS FOR HILLARY AVENUE SEWER

QUALITY PARAMETER	MAXIMUM (mg/L)	MINIMUM (mg/L)	ARITHMETIC MEAN (mg/L)	NUMBER OF SAMPLES
BOD <sub>5</sub>	167	20	126	12
COD	334	113	278	12
SS	169	92	137	12
VSS	137	63	112	12
TKN (as N)	50	12	30	11
NH <sub>3</sub> (as N)	28	7.8	18	11
NO <sub>2</sub> (as N)	0.7	0.01	0.1	11
NO <sub>3</sub> (as N)	0.3	0.1	0.1	11
TOTAL PHOSPHORUS (as P)	10	1.4	4.9	10
ALKALINITY (as CaCO <sub>3</sub> )	292	172	248	11
	MAXIMUM (NO./100 mL)	MINIMUM (No./100 mL)	GEOMETRIC MEAN (No./100 mL)	NUMBER OF SAMPLES
FECAL COLIFORM	$6.5 \times 10^6$	$0.7 \times 10^6$	$3.1 \times 10^6$	6
TOTAL COLIFORM	$1.5 \times 10^8$	$0.7 \times 10^8$	$1.2 \times 10^8$	6
ENTEROCOCCUS	$4.7 \times 10^5$	$0.9 \times 10^5$	$1.9 \times 10^5$	6

### Rainfall

Examination of raingauge charts indicated that the two installed rainfall gauges recorded approximately the same rainfall quantities at about the same time. As a result, the data from each gauge was combined by a straight averaging of rainfall for each hour.

Fifty rainfall events were registered during the summers of 1977 and 1978. The average results for 1977 and 1978 are tabulated in Table 2(A). When compared to the 30-year historical precipitation data (Table 2(B)), it can be seen that in 1977, the rainfall of each month was higher than the 30-year average for the corresponding month. The 1978 rainfall was the opposite; both the depth of rainfall and the number of days with rain were below the historical figures.

### Wet Weather Flow Quantity

#### Catchment And Sewer System Response

As mentioned earlier, the values of  $Q_{\max}$  and the total dry weather flow were 4,406 L/s and 360 L/s, respectively. The ratio of these quantities,  $4,406/360=12.3$ , indicates that an excessive quantity of combined sewage flows to the MTTS in wet weather. Typically, combined sewer systems are designed to accommodate 2.0-3.0 times the average dry weather flow.

During the study period, thirty-three storms produced inflow to the tank. The rainfall volume over the catchment area yielded by the 33 storms was  $3.89 \times 10^6 \text{ m}^3$ . The corresponding combined sewage volume, computed by the hydrograph method, was  $1.69 \times 10^6 \text{ m}^3$  of which  $1.53 \times 10^6 \text{ m}^3$  was stormwater runoff volume. The runoff to rainfall ratio was, therefore, 0.39. The distribution of the various flow volumes to the MTTS and the CSO tank during wet weather is shown in Figure 7.

TABLE 2

(A) SUMMARY OF OBSERVED DATA, 1977-1978

RAINFALL RECORDS

	JUNE		JULY		AUGUST		SEPTEMBER		OCTOBER		SEASONAL TOTAL	
	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978
MONTHLY RAINFALL (mm)	74.7	17.3	132.8	35.8	101.6	41.7	127.3	NO DATA	73.2	NO DATA	509.5	94.7*
NUMBER OF DAYS WITH RAINFALL	4	5	8	6	13	8	13	NO DATA	5	NO DATA	43	19*

(B) 30-YEAR AVERAGE RECORD AT NORTHCLIFF STATION, 1941-1970

	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	MEAN SEASONAL TOTAL
MEAN MONTHLY RAINFALL (mm)	64.3	81.3	71.4	59.7	63.5	340.1
NUMBER OF DAYS WITH RAINFALL	9	8	9	9	9	44

\* FOR JUNE TO AUGUST ONLY.

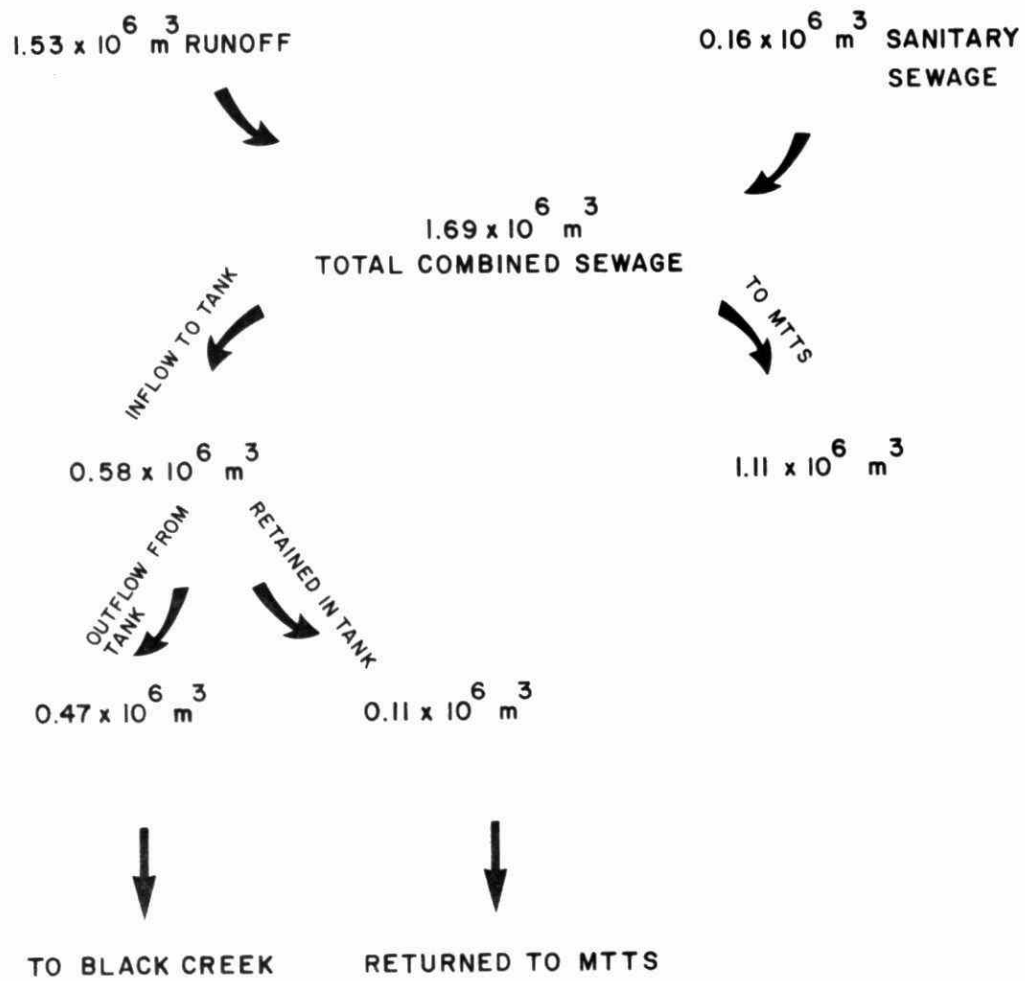


FIGURE 7: DISTRIBUTION OF FLOW VOLUMES IN EVENTS WITH TANK INFLOW

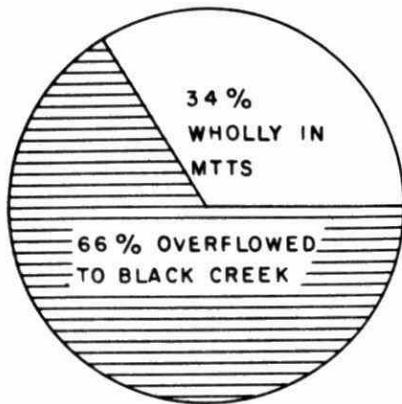


#### Volumetric Performance Of Tank

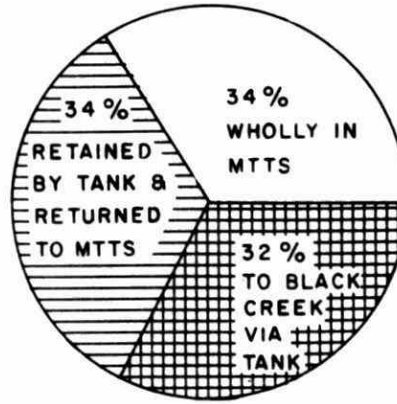
The total inflow volume to the tank was  $0.58 \times 10^6 \text{ m}^3$  and the overflow volume was  $0.47 \times 10^6 \text{ m}^3$ . The tank overflowed in 16 events.

Figure 8 summarizes the volumetric performance. It can be seen that the presence of the tank reduced the frequency of combined sewer overflow to the creek from 66% to 32% of all the 50 storm events. In respect of frequency, therefore, the improvement due to existence of the tank was significant.

Thirty-four percent of the catchment wet weather flow in all the events with tank inflow arrived at the tank and six percent was ultimately retained by the tank. This gives a ratio of retained volume to inflow volume of  $6\% \div 34\% = 18\%$ . This volumetric retention is somewhat disappointing. It should not, however, be used as the full measure of the tank performance. The acceptable retention ratio should ideally be determined on the basis of tank effluent quality, permissible pollutant loading and the permissible frequency of overflow to Black Creek. Since these criteria were not stipulated at the time of design, it is difficult to assess whether the tank performs adequately. Furthermore, although the study period extended over two summers, it is still limited in the context of hydrologic events. Consequently, any infrequent (and large) storm events may adversely affect the volumetric performance of the tank. Analysis over longer periods (say 10-20 years) would tend to minimize the impact of the infrequent events. In fact, in the study results, the storm on July 6, 1977 alone accounted for 43% of the tank total overflow volume in the entire study period. This storm had a return period between 50 and 100 years in terms of precipitation depth.

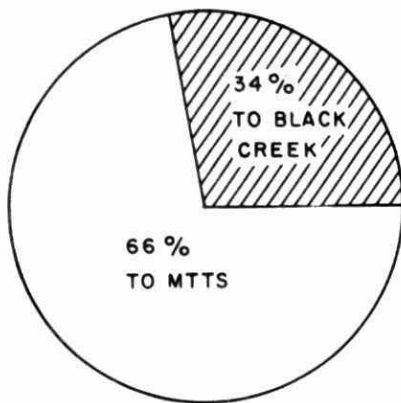


If tank not existing

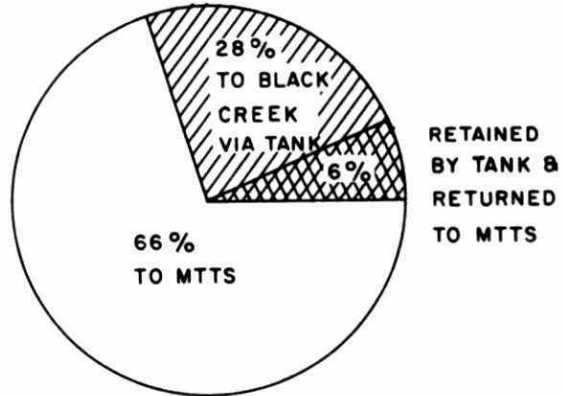


With tank existing

(A) FREQUENCIES



If tank not existing



With tank existing

(B) VOLUMES

FIGURE 8: VOLUMETRIC PERFORMANCE OF CSO TANK

The volumetric performance of the tank should also be viewed in the light of the policy for operating the tank. For example, the storm event on September 26, 1977 (Monday) produced an inflow volume of only 4,095 m<sup>3</sup> to the tank, but overflow from the tank occurred because the tank was not emptied after the storm event on the preceding Saturday.

#### Wet Weather Flow Quality

Although there were enough samples to give an indication of pollutant levels of the tank influent and effluent, simultaneous in/out quality data during the same storm were scarce. Concurrent influent and effluent quality data were obtained in only six events, numbers 7, 16B, 18, 20, 26 and 28. Except in event numbers 7 and 28, the tank overflow quality was generally better than the tank inflow quality, thereby indicating that tank retention helped to reduce pollutant levels. It is thought that in the case of storm numbers 7 and 28, quality samples of the tank overflow also contained flows from Black Creek which had backed up into the effluent channel. The fact that the tank overflow was visually much cleaner than the flow in Black Creek supports this opinion. The data of these two storms were rejected.

Storm number 26 was heavily polluted with average concentrations of BOD, COD, and SS ranging from 2 to 7 times the corresponding dry weather flow pollutant level. The high concentrations were felt to be due to scouring of the sewer.

The quality data of the four storms, numbers 16B, 18, 20 and 26 are listed in Table 3. The averages, including and excluding storm number 26, are presented for comparison. Since this is a very limited data base, the contribution of storm number 26 weighs heavily. As can be seen, the difference of average influent concentrations with and without this storm is very pronounced, whereas the effluent concentrations with and without this storm differ only slightly except for SS. Therefore, storm number 26 exerts a disproportionate influence upon the average removal efficiency.

TABLE 3

TANK INFLOW AND OUTFLOW QUALITY DATA

PARAMETER	(A) AVERAGES OF STORMS # 16B, 18, 20			(B) AVERAGES OF STORMS # 16B, 18, 20, 26		
	TANK INLET (mg/L)	TANK OUTLET (mg/L)	% REMOVAL *	TANK INLET (mg/L)	TANK OUTLET (mg/L)	% REMOVAL *
BOD	27.6	22.3	18.0	71.3	26.5	33.8
SS	166.0	137.3	15.7	383.5	233.8	24.2
NH <sub>3</sub> (as N)	0.56	0.77	(<0)	2.13	0.75	(<0)
TKN (as N)	4.9	4.7	3.3	10.9	5.0	22.5
TOTAL PHOSPHORUS (as P)	0.94	0.83	11.7	2.58	1.00	28.8

\*ARITHMETIC MEAN OF % REMOVAL OF CONSTITUENT EVENTS.

It should be noted that the average removal efficiencies listed in Table 3 are not derived from the average concentrations shown but are the average of removal efficiencies of each storm. The BOD and SS removal percentage indicated in Table 3 (B) compare favourably with the treatment efficiencies observed for the  $878 \times 10^3 \text{ m}^3$  detention facilities at Boston, Massachusetts (BOD and SS removal at 20% and 40%, respectively) (6).

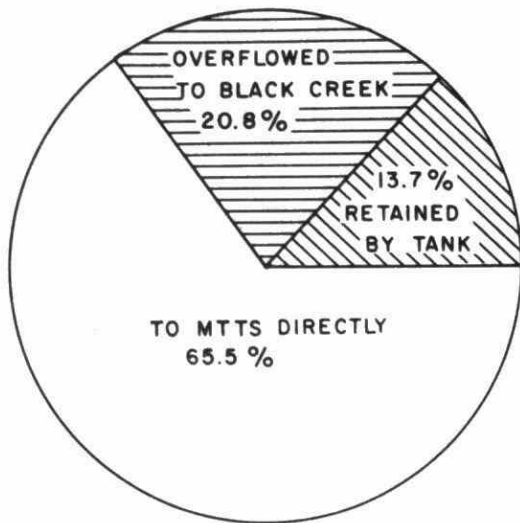
#### Reduction Of Pollutant Loads

Pollutant loading reduction by the tank for both wholly retained events and events with overflow was estimated. The volumes respectively of the total wet weather flow, the inflow to the tank and the overflow from the tank were taken from Figure 7. The tank's efficiency in removal of different types of pollutants for events with overflow was based on Table 3(B). It was assumed that the wet weather flow going to the MTTs and to the tank had the same quality. The computed results are illustrated in the pie charts in Figure 9.

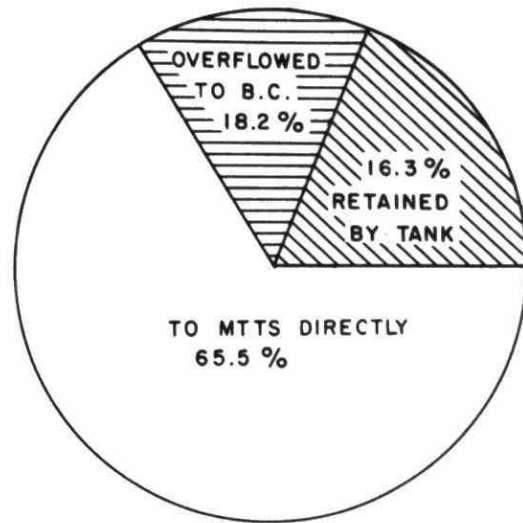
It can be seen from the pie charts that 65.5% of the pollutant load of each type flowed directly to the MTTs; the remaining 34.5% flowed to the tank. The pollutant loads wholly retained and/or removed during overflow periods by the tank ranged from 13.2% for TKN to 16.3% for BOD of the total influent loads. The corresponding load reduction percentages are 38% and 47%. These figures indicate that the tank is an effective device for reducing pollution from combined sewer overflow.

#### Bacterial Reduction

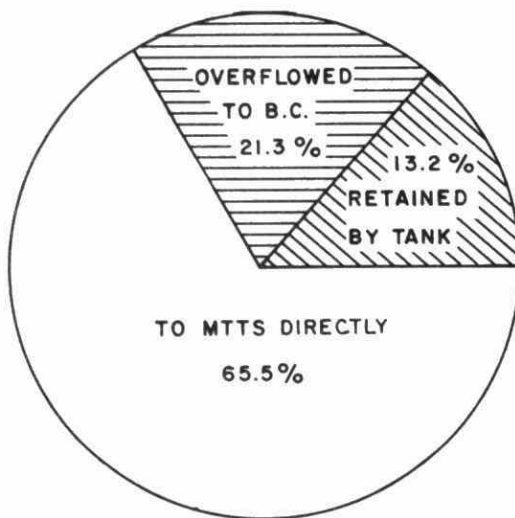
There was no adequate data for estimating bacteria reduction within the tank. However, due to the relatively short average retention time within the tank, little reduction through die-off was anticipated. Some reduction of seasonal bacterial loading was of course achieved because of the events wholly retained within the tank.



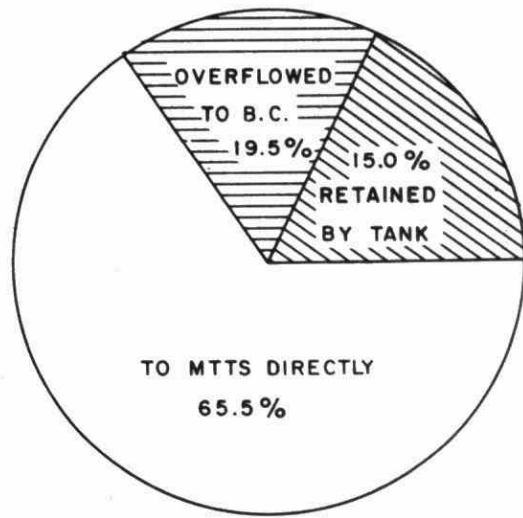
(A) SUSPENDED SOLIDS



(B) BOD



(C) TKN



(D) TOTAL PHOSPHORUS

FIGURE 9: POLLUTANT LOAD REDUCTION BY CSO TANK IN ALL EVENTS WITH TANK INFLOW

#### Long-Term Performance

As already noted, the performance of a CSO tank should ideally be viewed also in the long-term. One means for doing so is model simulation. Some simulation results using the STORM model for this CSO tank for the precipitation of years 1970-76 were reported (7). However, as the model study was preliminary, the results are not included in this paper. More model simulation work for this CSO tank will be carried out under a current study: the Toronto Area Watershed Management Study.

#### Operation And Maintenance

Based on visual observations, the average quantity of sediment collected in the tank per storm was about 100 mm thick spread over the tank bottom. The sediment was a gelatinous material with some wood and paper mixed with it. The sediment would dry out between storms and become flaky and dusty. No odour problem was observed.

The fine particles of the sediment, like mud and silt, were removed by hosing them down to the MTTS via the under-drain of the tank. The coarse particles were allowed to accumulate until there was a large enough quantity for removal. They were removed by shovelling, then lifted to the surface and hauled away by truck. Each tank cleaning operation required 4 to 6 workers working for an average of 4 days. The operation appeared to be cumbersome and labour intensive, but any equipment or construction that may help improve the operation is unlikely to be cost-saving as well.

When the tank was full and overflowing, there was considerable floating material in the tank. Most of this material was kept behind the floatables barrier at the effluent end of the tank, so that very little floating material escaped to Black Creek. The barrier thus greatly enhanced the aesthetic quality of the overflow to the creek.

In general, it may be said that the detailing of the tank appurtenances and the operation and maintenance of the tank, all of which are necessary for the successful application of a CSO tank, were attended to quite appropriately.



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TOXICITY OF ACID AND ALUMINUM TO EARLY  
DEVELOPMENTAL STAGES OF RAINBOW TROUT  
(Salmo gairdneri Richardson)

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ABSTRACT

TOXICITY OF ACID AND ALUMINUM TO EARLY DEVELOPMENTAL  
STAGES OF RAINBOW TROUT

Laboratory studies were conducted to study the effects of inorganic aluminum ( $0.02$  to  $1.0 \text{ mg L}^{-1}$ ) and pH ( $4.5$  to  $7.2$ ) on the survival of early developmental stages of rainbow trout (Salmo gairdneri). Trout became more sensitive to aluminum but less sensitive to hydrogen ion with progressive levels of development (cleavage egg < eyed egg < yolk sac fry < swim up fry). Nominal total aluminum concentrations as low as  $0.5 \text{ mg L}^{-1}$  at pH  $5.5$  and  $0.1 \text{ mg L}^{-1}$  at pH  $4.5$ , were acutely toxic to yolk sac and swim up fry stages while survival and development of cleavage embryos were not adversely affected at aluminum concentrations as high as  $1.0 \text{ mg L}^{-1}$  at all pH levels tested. The presence of aluminum was beneficial to the survival of cleavage embryos at pH  $4.5$ , reducing mortality from  $27.5\%$  in the control ( $<0.02 \text{ mg L}^{-1} \text{ Al}$ ) to  $4.5\%$  at high aluminum ( $1.0 \text{ mg L}^{-1}$ ). Latent toxic effects of pH and aluminum were evident for trout in the eyed embryo stage following transfer to control conditions.

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## INTRODUCTION

Hydrogen ion ( $H^+$ ) toxicity has recently been linked to the disappearance or decline of fish populations via the process of environmental acidification (1,2,3,4). Marked increases in  $H^+$  ion concentrations have been observed during spring and fall runoff periods (5,6,7,8), and have caused death in fish (4,9,10). Levels of pH however that have been reported to be lethal to fish in acidified waters in the field, are generally higher (5.0 to 6.0) than estimates of lethal pH levels determined under laboratory conditions (11,12), which suggest that additional stress factors must be present in natural systems.

The decreased pH of precipitation due to strong acids ( $H_2SO_4$ ,  $HNO_3$ ), has resulted in the increased mobilization of metals, particularly aluminum, from soils (13,14). This has resulted in changes of both the concentration and forms (15) of aluminum that have been observed in low alkalinity, ionic strength waters in parts of New York state (16), Norway (17,18), Nova Scotia (19) and Ontario (8). Observations of Cronan and Schofield (16), indicated that higher concentrations of aluminum in acid stressed waters could be detrimental to fish health.

Aluminum was found to be acutely toxic to brook trout (Salvelinus fontinalis) in low pH (4.2 to 5.6) and calcium ( $<2.0 \text{ mgL}^{-1}$ ) waters at concentrations as low as  $0.2 \text{ mgL}^{-1}$  (16,20). Chemical characterization of aluminum identified the labile monomeric inorganic fraction as the most toxic form (15). Acute toxic effects of aluminum at concentrations up to  $200 \text{ mgL}^{-1}$  were not observed at pH 6.0 to 7.0 in laboratory tests with rainbow trout (Salmo gairdneri), although the tests were conducted with older fry stages and under different water quality conditions (21,22). Laboratory studies with brook trout and white sucker (Catostomus commersoni) have demonstrated differences in both species and life stage sensitivities to aluminum (20). The early fry stages were more sensitive to aluminum than eggs. The study, however, did not include a comparison of early and late egg stages, which have been shown to differ in their relative sensitivities to low pH (23).

Death of fish in acidified waters has been attributed in part to the impaired regulation of body salts (24). Decreased levels of plasma  $Na^+$  and  $Cl^-$  were observed in brown trout (Salmo trutta), subjected to  $0.9 \text{ mgL}^{-1}$

aluminum at pH 5.0 and 5.5 (25). However the effects of combined pH and aluminum stress on whole body electrolytes including  $\text{Na}^+$ ,  $\text{Cl}^-$ , as well as  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  have not previously been examined.

The present laboratory studies were designed to identify stages of fish development that would be most affected by short term exposure to elevated concentrations of aluminum and hydrogen ion. Rainbow trout were exposed for 8 days during the cleavage egg, eyed egg, yolk sac fry and swim up fry stages to aluminum ( $0.02$  to  $1.0 \text{ mgL}^{-1}$ ) at different pH levels ( $4.5$  to  $7.2$ ). A 12-day recovery period was provided following the test exposure to identify latent toxicity. A second series of experiments were conducted with trout fry to determine their ability to maintain normal body electrolyte levels in the presence of aluminum ( $0.4 \text{ mgL}^{-1}$ ) at sublethal pH levels ( $5.0$  to  $6.0$ ).



## MATERIALS AND METHODS

### Fish Stocks

Newly fertilized eggs of rainbow trout (Salmo gairdneri Richardson) were obtained from two local certified disease-free fish hatcheries. The eggs were reared to the swim-up fry stage in vertical flow incubation chambers, supplied with 10°C dechlorinated Lake Ontario tap water at a rate of 13 to 16 L min<sup>-1</sup> (Appendix I). The eggs were inspected periodically and dead eggs were removed to minimize fungal growth. Rates of development and percent mortalities of trout reared to swim-up, were similar for the different stock populations.

### Experimental Conditions

The experiments were conducted in artificially softened water (Ca<sup>++</sup> ~4.0 mgL<sup>-1</sup>, ionic strength ~0.7 mmolL<sup>-1</sup>), obtained by dilution of the dechlorinated tap water with an appropriate amount of reverse osmosis-treated tap water (Appendix I).

The pH of the test solution was adjusted and maintained using sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Nominal total aluminum concentrations were achieved by addition of stock solutions of analytical grade aluminum sulphate [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O] and waters were aged for 24 hours prior to the addition of fish. Measured pH levels rarely exceeded 0.2 units of nominal test levels.

The control and test solutions were aerated at a rate of 5-10 ml L<sup>-1</sup> min<sup>-1</sup> to provide continuous mixing and to maintain dissolved oxygen levels near saturation. The experiments were conducted at 10±1°C. Light intensity 10 cm above the water surface, ranged from 10-20 lux during a 14-hour light period.

Water samples were withdrawn from all solutions after 0 and 96 hours of testing for determinations of pH, alkalinity, SO<sub>4</sub><sup>=</sup> and total unfiltered aluminum. Water hardness, major ion (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, Cl<sup>-</sup>, F<sup>-</sup>) and trace metals (Cd, Cr, Cu, Co, Ni, Mn, Zn, Pb) were measured at the beginning of each test and after renewal of the test solutions. Chemical analyses were performed by the Ontario Ministry of the Environment, Laboratory Services Branch, according to the procedures described in Outlines of Analytical Methods (1981).

The relative concentrations of aqueous inorganic aluminum species (i.e. hydroxides, fluorides, sulphates) were calculated from nominal aluminum concentrations, measured water chemistry parameters and thermodynamic constants, derived for aluminum in equilibrium with micro-crystalline gibbsite (pers. comm. Bruce Lazerte, University of Guelph, Ontario/Ontario Ministry of the Environment).

Concentrations of dissolved organic carbon in the test water were low ( $0.4 \text{ mgL}^{-1}$ ). Preliminary analyses for aluminum suggested that all or most of the aluminum existed as either suspended or dissolved inorganic aluminum forms.

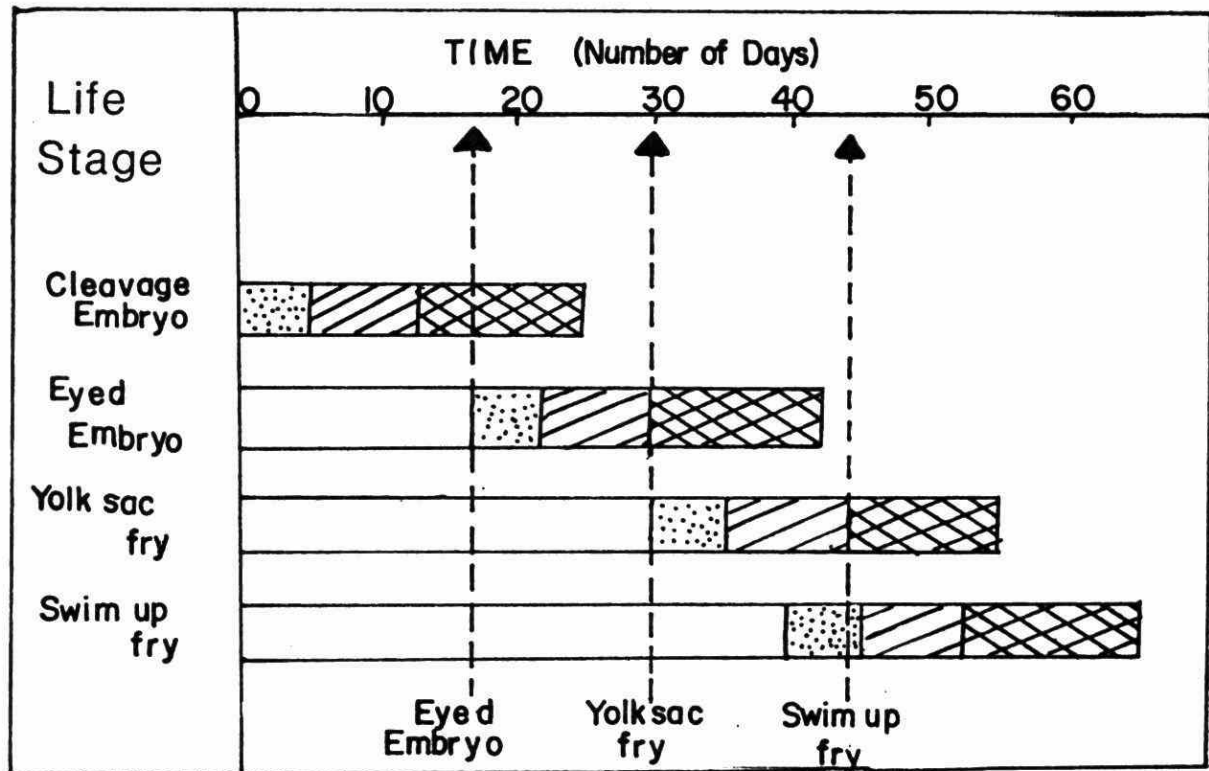
#### Life Stage Sensitivity Comparison

Four successive early developmental stages of rainbow trout, were selected for comparison of their relative sensitivities to aluminum and pH. Exposure of the cleavage embryo, eyed embryo, yolk sac fry and swim up fry stages were initiated 1, 17, 30 and 42 days after fertilization, respectively (Fig. 1). The experiments were divided into three exposure periods: acclimation, test and recovery. Eggs and fry were held in the test water under control conditions ( $\text{Al} = 0.02 \text{ mgL}^{-1}$ ;  $\text{pH} = 7.2$ ) for five days prior to testing. Each stage was then exposed for eight days, to nominal aluminum concentrations of  $<0.02$  (control), 0.1, 0.5 and  $1.0 \text{ mgL}^{-1}$  and pH levels of 7.2, 6.5, 5.5 and 4.5. The  $0.1 \text{ mgL}^{-1}$  aluminum concentration was not included in the concentration series conducted at pH 7.2. The tests were conducted under static conditions with 100% renewal of the test solution after four days. Eggs and fry that remained alive at the end of the test were returned to "control" conditions and held for an additional twelve days.

All developmental stages were tested in modified embryo-larval rearing chambers (26). The exposure chambers (Fig. 2) were designed to retain a sufficient volume of water (50 mL) when removed from the test solution in order to minimize handling stress during transfer. Two chambers, each containing 35 organisms were immersed in 10 to 15 L of test solution in each of two, 25L cylindrical plastic tanks.

The criteria for death were discolouration of the egg membrane and cessation of the heart in the post-hatching fry stages. Discoloured cleavage eggs were cleared in 10% acetic acid to differentiate between fertilized and non-fertilized eggs.

Fig. 1 EMBRYO/ALEVIN EXPOSURE SEQUENCE



**INCUBATION**



**ACCLIMATION (5 days)**

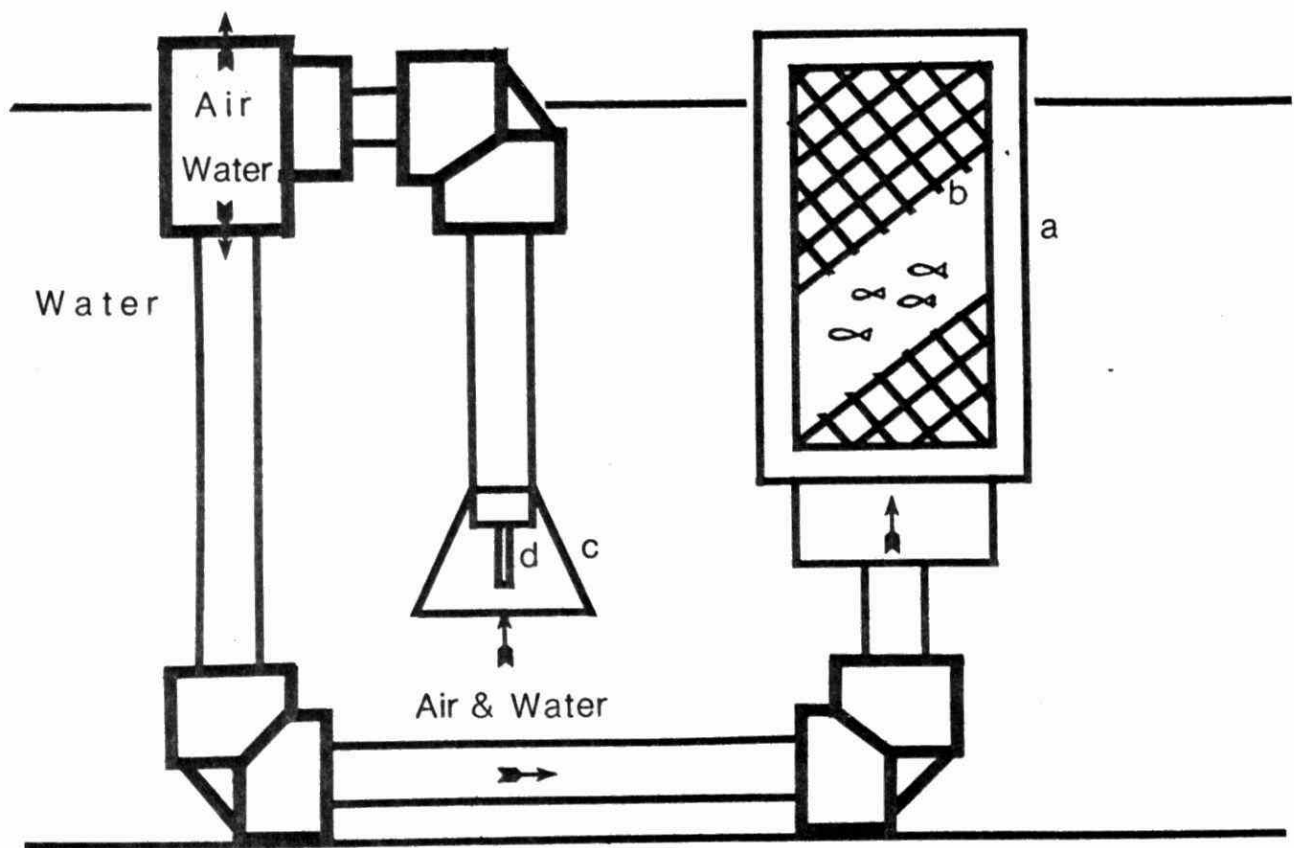


**TEST (8 days)**



**RECOVERY (12 days)**

Fig. 2 System Used For Exposing Egg and Fry Stages of Rainbow Trout to Test Conditions



(a) Plastic Test Chamber

(c) Funnel

(b) Nylon Screen

(d) Airline

#### Determination of Electrolyte Levels

Whole body electrolytes ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ) were determined in rainbow trout exposed to control ( $0.02 \text{ mgL}^{-1}$ ) and high ( $0.4 \text{ mgL}^{-1}$ ) aluminum concentrations at three pH trials (6.0, 5.5, 5.0). Alevin rainbow trout were held in test water (ionic strength  $0.7 \text{ mmolL}^{-1}$ , pH 7.2, Al  $<0.02 \text{ mgL}^{-1}$ ) for 60 days prior to the test. The fish were fed EWOS trout feed at a rate of 4% of total body weight per day. Feeding was discontinued 24 hours prior to the test and for the duration of the 96 hour test period.

Ten alevins (0.5 to 2.0 gm) were placed into each of two, 25L plastic cylindrical tanks containing 20 L of test solution. The tests were carried out under static conditions.

Electrolyte levels ( $\bar{x} \pm \text{S.D.}$ ) were determined from three, two-fish composite samples and were reported as  $\text{mmol} \cdot 100\text{g}^{-1}$  wet weight. Fish subjected to the high aluminum ( $0.4 \text{ mgL}^{-1}$ ) treatments at pH 5.5 and 5.0 were removed prior to death (after 48 hours), for determination of electrolyte levels. Fish from the remaining treatments were removed at the end of the 96 hour test period.

Body  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were determined in the aluminum exposed fish tested at pH 6.0, 5.5 and 5.0, while body  $\text{Cl}^-$  levels were measured in the aluminum exposed fish from the pH 5.5 trial only. Cation levels were determined by atomic absorption spectrophotometry and  $\text{Cl}^-$  levels were analysed by ion chromatography (Laboratory Services Branch, Ontario Ministry of the Environment).

#### Data Analysis

Hatch and mortality data were subjected to arcsine transformation and compared for differences using one way analysis of variance. Mean values for whole body  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{K}^+$  concentrations were compared for differences using one way analysis of variance with pairwise comparisons of the treatment means according to Scheffe's S Method.

### RESULTS

#### Life Stage Sensitivities to Aluminum/pH

Rainbow trout became more sensitive to aluminum but more tolerant to

Fig. 3 RELATIVE SENSITIVITIES OF THE CLEAVAGE EGG, EYED EGG, YOLK SAC FRY AND SWIM UP FRY STAGES OF RAINBOW TROUT TO ALUMINUM AT DIFFERENT pH LEVELS

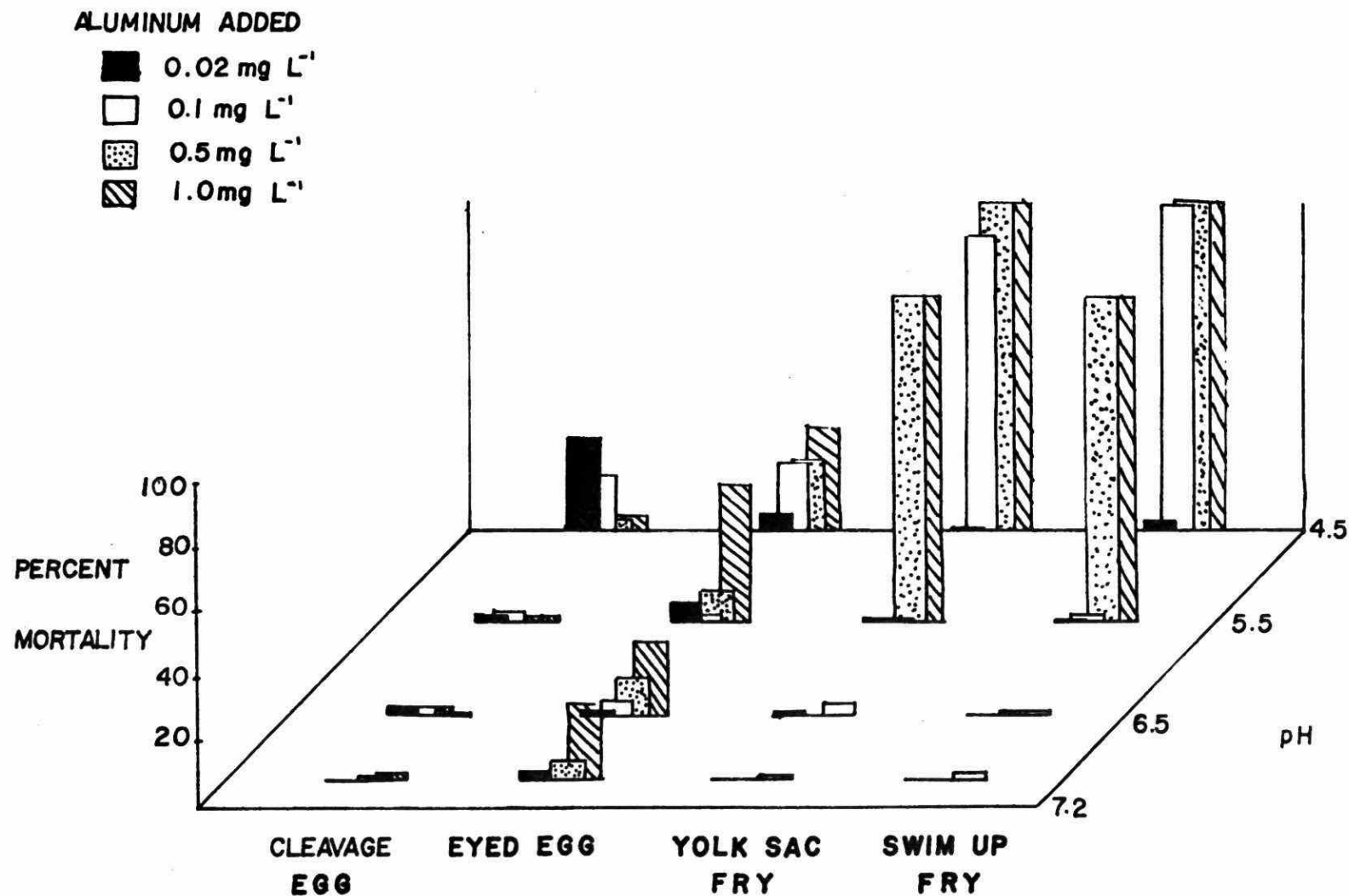


Fig. 4 Percentage Hatch of Trout Subjected for 8 Days to Aluminum at Different pH Levels During the Eyed Egg Stage

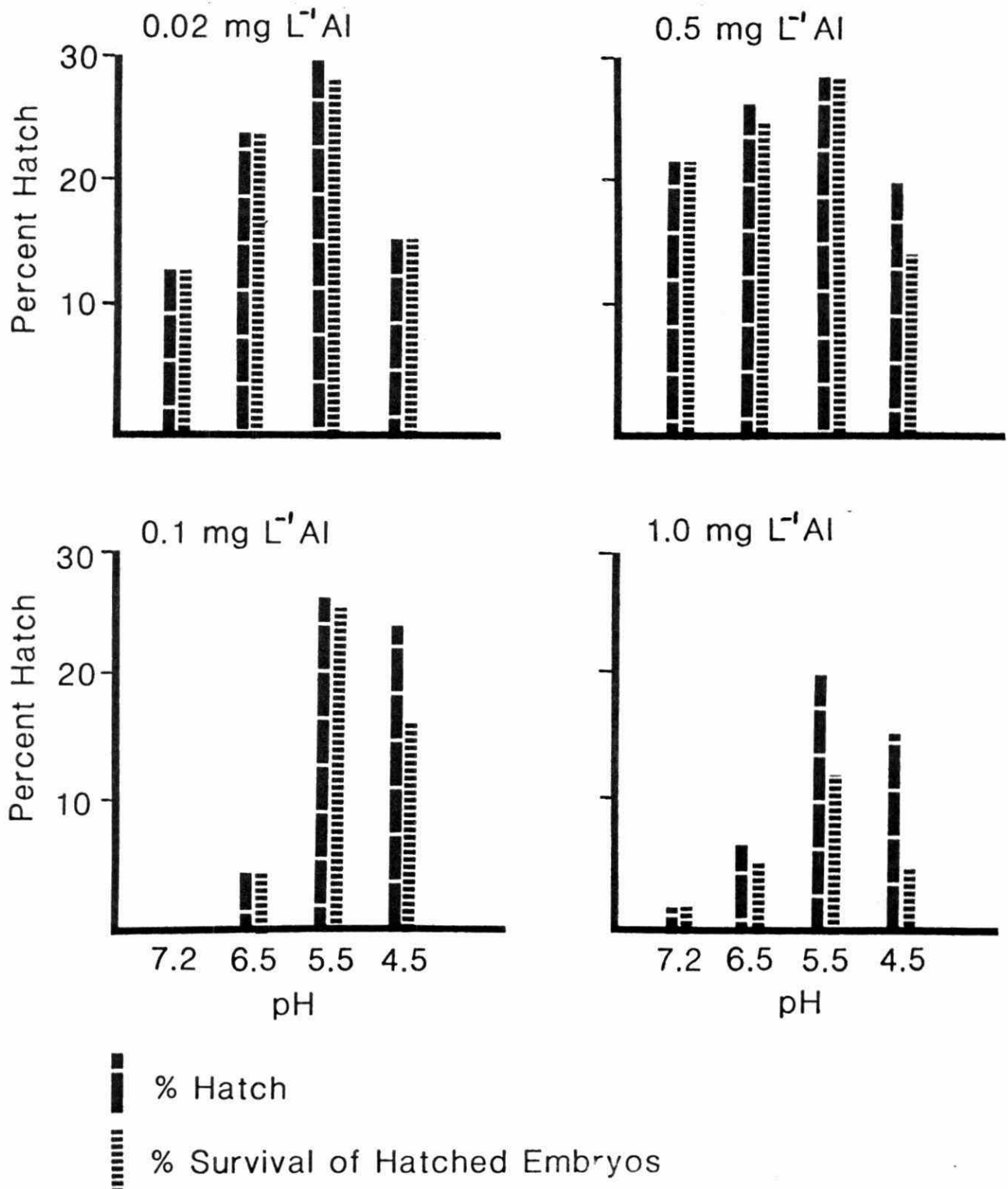


Table 1: Mortality ( $\bar{x}$  and 95% C.I.) of eyed embryos subjected to pH and aluminum after test (8 days) and recovery (12 days) periods.

pH	Aluminum Added (mg L <sup>-1</sup> )	N	Cumulative Percent Mortality	
			Test (C.I.)	Recovery (C.I.)
7.2	<0.02	137	2.9 (0.7- 7.2)	4.5 (1.6- 9.1)
	0.05	138	5.8 (2.5-11.1)	56.0(47.1-64.2)
	1.0	141	14.5 (6.6-17.8)	52.6(43.0-60.9)
6.5	<0.02	140	1.4 (0.2- 5.0)	11.3 (6.7-17.9)
	0.1	140	4.3 (1.6- 8.9)	15.5(10.1-22.8)
	0.5	140	10.7 (6.1-17.1)	49.4(40.7-57.9)
	1.0	139	21.6(15.1-29.4)	46.4(37.6-54.7)
5.5	<0.02	138	5.8 (2.5-11.1)	30.9(23.6-39.6)
	0.1	138	2.2 (0.4- 6.2)	20.9(14.5-28.8)
	0.5	140	10.0 (5.6-16.2)	35.5(27.8-44.2)
	1.0	141	43.4(34.9-51.9)	84.8(78.1-90.5)
4.5	<0.02	140	5.7 (2.5-10.9)	27.4(20.0-35.3)
	0.1	135	21.5(14.9-29.4)	33.3(25.5-42.0)
	0.5	141	22.7(16.0-30.5)	49.8(41.1-58.2)
	1.0	138	31.9(24.2-40.3)	67.1(58.9-75.1)



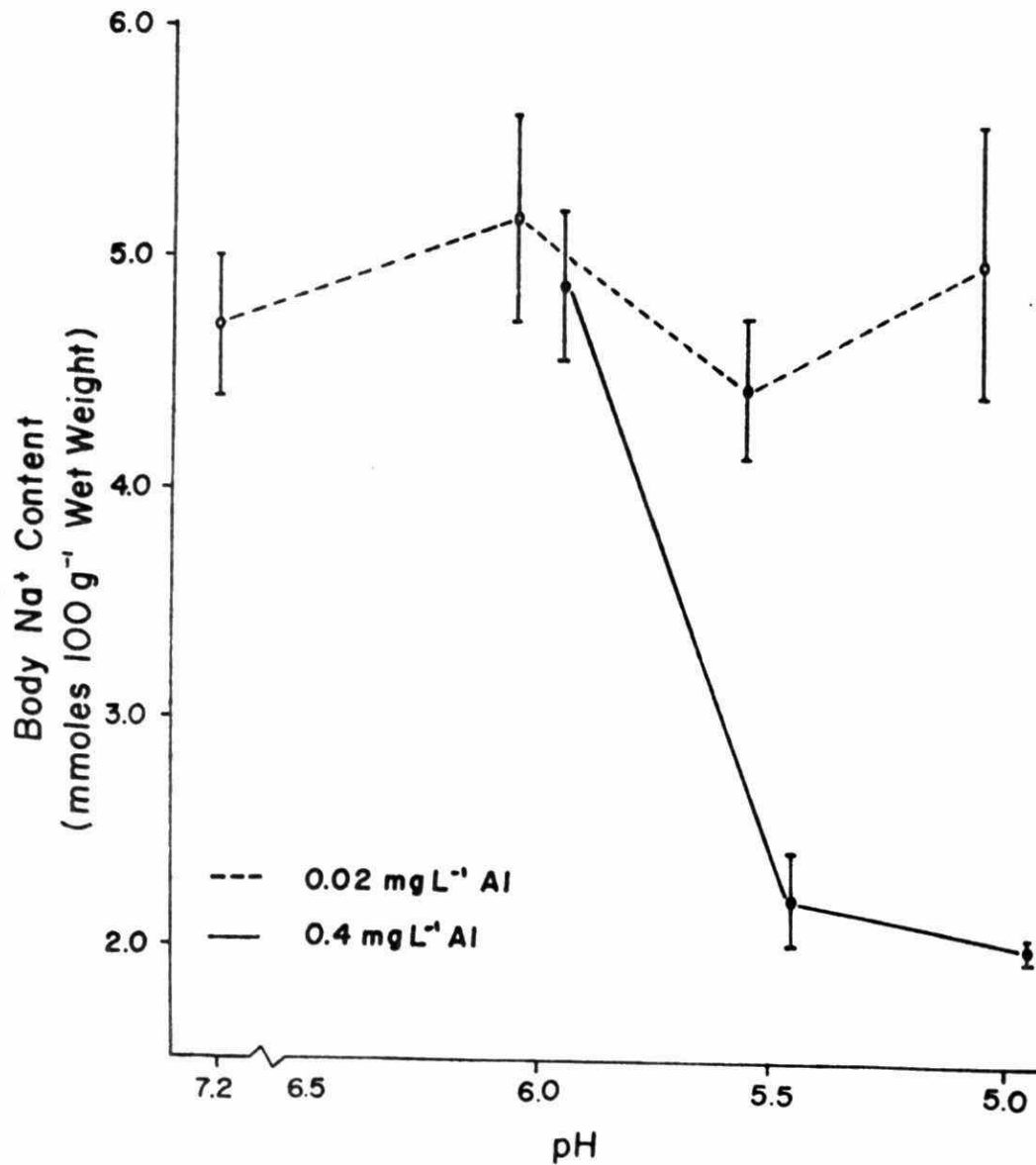
hydrogen ion with progressive level of development (cleavage egg < eyed egg << yolk sac fry ≈ swim up fry). Survival and development of the cleavage egg (five day old embryos), yolk sac and swim up fry stages were unaffected (mortality <5%) after eight days exposure to nominal aluminum concentrations as high as  $1.0 \text{ mgL}^{-1}$  at pH 7.2 and 6.5 (Fig. 3). Eyed eggs were moderately sensitive to aluminum at these pH levels, experiencing 14.2 to 21.6% mortality at high aluminum ( $1.0 \text{ mgL}^{-1}$ ). For all other stages tested, aluminum toxicity increased with decreasing pH. Post-hatching fry stages demonstrated the greatest sensitivity to aluminum at low pH. Percent mortality of yolk sac and swim up fry, exceeded 90% at aluminum concentrations of  $\geq 0.5 \text{ mgL}^{-1}$  at pH 5.5 and  $\geq 0.1 \text{ mgL}^{-1}$  at pH 4.5. Eyed eggs were less sensitive to aluminum ( $1.0 \text{ mgL}^{-1}$ ) than fry, with mortalities ranging from 31.9 to 43.3% at pH levels of 5.5 and 4.5 respectively.

Eyed trout eggs experienced enhanced hatching rate in the lower pH waters (6.5, 5.5, 4.5) relative to the near neutral (pH 7.2) water for all aluminum concentrations during the 8 day test period (Fig. 4). No effect of aluminum on hatching rate was apparent. However, significant ( $p < 0.05$ ) mortalities of both eggs and fry continued to occur during the recovery period at all pH and aluminum treatment levels, relative to the controls (pH 7.2, Al  $< 0.02 \text{ mgL}^{-1}$ ) (Table 1). Latent toxic effects of either pH or aluminum were not evident for the other stages tested.

#### pH/Aluminum Effects on Whole Body Electrolyte Levels

The loss of electrolytes, in particular  $\text{Na}^+$  and  $\text{Cl}^-$ , determined in fish subjected to elevated aluminum ( $0.4 \text{ mgL}^{-1}$ ) in solutions ranging in pH (6.0 to 5.0) closely paralleled the pattern of mortality (Appendix II). Alevin rainbow trout maintained normal body ~~content~~ levels of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  when exposed to low pH (6.0 to 5.0) and aluminum concentration ( $< 0.02 \text{ mg L}^{-1}$ ). However, marked reductions in body content levels of  $\text{Na}^+$  (Fig. 5) and  $\text{Cl}^-$  and to a lesser extent  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were observed at high aluminum ( $0.4 \text{ mgL}^{-1}$ ). The extent of the loss varied with the ion being measured and increased with decreasing pH. Reductions in body ~~Na~~<sup>+</sup> (58.8 to 61.8%),  $\text{K}^+$  (16.9 to 20.0%),  $\text{Ca}^{++}$  (17.4 to 19.6%) and  $\text{Mg}^{++}$  (18.2 to 20.0%) were greatest at pH 5.0. Ion loss was not reduced at pH 6.0.

FIG. 5: Mean Whole Body Sodium ( $\text{Na}^+$ ) Levels in Alevin Rainbow Trout Exposed to Aluminum at Different pH Levels



## DISCUSSION

### Life Stage Sensitivities to Aluminum/pH

Embryos in cleavage stage were more sensitive to low pH (4.5) than older embryonic and fry stages. Similar results have been noted for brook trout, and white sucker (20). Atlantic salmon (Salmo salar) embryos in early cleavage were more sensitive than older encapsulated stages but were less sensitive than fry (12). These authors suggested that the greater tolerance of the encapsulated egg was due to the presence of the surrounding perivitelline fluid and zona radiata. The egg membrane, however, did not represent an effective barrier to  $H^+$  ion in experiments conducted with atlantic salmon embryos (27). The pH of the perivitelline fluid was observed to decrease rapidly when embryos were exposed in acid waters (pH 5.5, 4.0).

Reasons for the greater sensitivity of the embryonic stages are not yet known. In older fish, exposure to low pH has been shown to interfere with the regulation of body salts, in particular,  $Na^+$  and  $Cl^-$  (24,28). Daye and Garside (29) suggested that the death of pre-hatching embryos exposed to low pH, resulted from injury of the integument which is the principle site of respiration and ion exchange in the embryo (30). Histological examinations of the yolk sac epithelium of rainbow trout embryos in early development, showed fewer numbers of cell types with the capability for ionoregulation than older embryonic stages (30). The greater sensitivity to low pH of the cleavage embryo may in part be related to a more limited capacity to regulate ion levels.

Sensitivity of trout to aluminum, on the other hand, increased with progressive level of development, suggesting that the zona radiata and/or perivitelline fluid associated with the egg stages provided an effective barrier to aluminum ion. Older encapsulated embryos showed increasing sensitivity to aluminum. A similar response was observed for zebrafish embryos (Brachydanio rerio), subjected to zinc (31). The author noted that the egg membrane became increasingly brittle with time, suggesting that a change in the integrity of the membrane might also be accompanied by an increasing permeability to metal ions.

Aluminum was more toxic in solutions of decreasing pH for all stages except the cleavage embryo. In this case the toxic effects of low pH (4.5)

were mitigated by aluminum, possibly in response to the presence of free aluminum ( $\text{Al}^{3+}$ ). Differences in the relative sensitivities of the various life stages to aluminum were most pronounced at pH levels of 5.5 and 4.5. Development and survival of the cleavage embryo were unaffected by nominal aluminum concentrations as high as  $1.0 \text{ mgL}^{-1}$  while survival of the yolk sac and swim up fry was significantly reduced ( $p < 0.01$ ) in the presence of  $0.5 \text{ mgL}^{-1}$  and  $0.1 \text{ mgL}^{-1}$  Al at pH 5.5 and 4.5 respectively. Survival of the eyed embryo was only moderately reduced at high aluminum ( $1.0 \text{ mgL}^{-1}$ ) although latent toxic effects of both pH and aluminum were evident during the recovery period.

The increase in aluminum toxicity observed at lower pH (4.5 to 5.5) was likely due to changes in the relative concentrations of aqueous inorganic aluminum species. Aluminum was most toxic to trout at pH 4.5. Under these conditions, free aluminum, aluminum hydroxide and aluminum fluoride complexes dominated ( $\text{Al}^{3+} > \text{AlOH}^{2+} > \text{AlF}^{2+} > \text{Al}(\text{OH})_2^+ > \text{AlF}_2^+$ ; pers. comm. Bruce Lazerte). At the higher pH levels there is a shift to higher ( $\text{OH}_x$ ) ligands of aluminum, and a general reduction in the total dissolved aluminum because of its decreased solubility. At pH 7.2, the  $\text{Al}(\text{OH})$  species appear to dominate. However, no acute toxic effect was observed at this pH.

#### Effects of pH/Aluminum on Electrolyte Levels

Loss of electrolytes has been observed in fish subjected to "severe" acid stress. Packer and Dunson (28) observed up to 60% reductions in body  $\text{Na}^+$  content of rainbow trout exposed to lethal pH (3.5). They suggest that the loss of  $\text{Na}^+$  occurred in response to greatly increased  $\text{Na}^+$  efflux rate and to a lesser extent, to a decreased rate of  $\text{Na}^+$  influx. In laboratory and field studies Leivestad et al (24) noted decreased levels of plasma  $\text{Na}^+$  and  $\text{Cl}^-$  in brown trout severely stressed by low pH (4.0). More recent studies (25), revealed similar effects in brown trout subjected to low but sublethal pH (5.0-5.5) in the presence of elevated aluminum concentrations. Similarities in the nature and extent of the response to lethal (pH < 4.0) versus sublethal pH/elevated aluminum was seen as suggestive that the fish gill, which appears to be the primary target site, is unable to distinguish between the two stress factors.

Results of the present study demonstrated that whole body content levels of inorganic ions decreased in response to aluminum at sublethal pH levels.

Death of alevin rainbow trout subjected to elevated aluminum ( $0.4 \text{ mgL}^{-1}$ ) in acid solutions (pH 5.5 to 5.0) was preceded by marked reductions in whole body  $\text{Na}^+$  and  $\text{Cl}^-$  while lower but significant ( $p < 0.05$ ) reductions in  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were also observed. The ion loss was greatest at pH 5.0. Alevins however, showed no observable signs of stress at pH values as low as 5.0 in the absence of aluminum ( $< 0.02 \text{ mgL}^{-1}$ ) and were capable of maintaining normal electrolyte levels.

#### SUMMARY

- (1) Sensitivity of rainbow trout to hydrogen ion decreased with increasing level of development (cleavage egg > eyed egg > yolk sac fry  $\approx$  swim up fry).
- (2) Sensitivity to aluminum varied with pH and developmental stage.
  - (a) Aluminum was generally more toxic in acid solutions (pH 4.5 to 5.5).
  - (b) Trout were most sensitive to aluminum during the yolk sac and swim up fry stages and least sensitive during the cleavage egg stage.
  - (c) Aluminum was beneficial to survival of cleavage embryos at pH 4.5.

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APPENDIX I: Chemical Characteristics of incubation and test waters.

Parameter (mg L <sup>-1</sup> )	Incubation Water		Test Water	
	Mean	S.D.	Mean	S.D.
Ionic Strength <sup>1</sup>	5.4		0.7	
Hardness <sup>2</sup>	113.8	6.71	14.3	1.38
Ca	32.5	2.46	4.2	0.37
Mg	7.8	0.24	0.9	0.15
Na	13.4	0.93	2.9	0.18
K	1.6	0.09	0.7	0.11
Cl	30.5	0.50	4.8	0.20
F	0.9	0.04	0.1	0.01
DOC	1.6	0.08	0.4	0.25
DIC	0.8	0.52	0.9	0.32
NH <sub>3</sub>	0.091	0.0272	0.118	0.0584
NO <sub>2</sub>	0.002	0.0013	0.002	0.0013
NO <sub>3</sub>	0.416	0.0527	0.16	0.0177
Fe	0.013	0.0058	0.017	0.0115

Cu, Ni, Zn, Cd, Co, Cr, Pb, Mn at or below Detection Limits (<0.001)

<sup>1</sup>mgL<sup>-1</sup> as CaCO<sub>3</sub>

<sup>2</sup>mmoles L<sup>-1</sup>

APPENDIX II: Mean whole body electrolyte levels (m moles 100g<sup>-1</sup> wet weight) in rainbow trout alevins exposed to combinations of aluminum and pH.

pH	Al (mg L <sup>-1</sup> )	Na <sup>+</sup>		K <sup>+</sup>		Ca <sup>++</sup>		Mg <sup>++</sup>		Cl <sup>-</sup>	
		$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.
7.2	<0.02	4.49	0.126	8.11	0.19	9.0	1.54	0.96	0.025		
6.0	<0.02	5.15	0.452	8.62	0.19	10.36	0.37	0.99	0.041		
6.0	0.40	4.86	0.331	8.11	0.074	8.62	0.57	0.95	0.041		
7.2	<0.02	4.57	0.574	7.47	0.412	11.29	0.38	1.02	0.025	3.09	0.29
5.5	<0.02	4.42	0.331	7.25	0.451	11.38	0.33	0.96	0.119	4.14	0.43
5.5	0.40	2.21*	0.213	6.51**	0.374	10.40	0.65	0.89	0.091	2.07**	0.19
7.2	<0.02	4.70	0.305	8.50	0.410	8.17	0.49	1.03	0.053		
5.0	<0.02	4.93	0.665	8.32	0.443	8.5	0.63	1.04	0.025		
5.0	0.40	2.03*	0.052	6.88**	0.257	6.83**	0.19	0.85	0.025		

\*Significant difference (p<0.05)

\*\*Significant difference (p<0.01)



Ontario

- 270 -

Ministry  
of the  
Environment

SUBLETHAL EFFECTS OF ACID AND ALUMINUM EXPOSURE  
ON JUVENILE RAINBOW TROUT

Christine Neville

First Stage Summary

This report is a summary of the first stage of a study on the physiological response of juvenile fish to environmental acidification. It deals with the response to sublethal concentrations of the most toxic species of aluminum, - monomeric inorganic aluminum.

Juvenile rainbow trout (200-400 g) were exposed to pH values of 6.1, 5.0, 4.5 and 4.0 with (experimental group) and without (control) 75 ppb monomeric inorganic aluminum, for up to eleven days under resting conditions. Ventilatory data were recorded daily. Blood gas and acid-base data, and blood and muscle tissue electrolytes were measured on the last day of exposure. Tissue from the gills, liver, kidney, intestine, and gonads were examined for aluminum concentrations and histopathology. A few fish died before the end of the exposure period. Subsequently, blood and tissue samples were taken from any other fish in the same group that appeared to be succumbing, before they became moribund. Mean exposure times for three experimental groups were approximately 8 days (pH 6.1, 4.5 and 4.0) and for one control group (pH 4.0) was only 3 days.

In the experimental fish, aluminum was deposited on the gills but did not accumulate in the internal organs. Gill aluminum concentrations were highest at pH 6.1 and lowest at pH 4.0. Ventilation and cough rates were high at pH 6.1, 4.5 and 4.0. Oxygen consumption increased at pH 4.5 and 4.0 but was reduced at pH 6.1 despite the high ventilation rate. Consequently arterial blood oxygen saturation levels were very low at pH 6.1 but were only slightly reduced in the other pH groups. However, in the lower pH groups, acidosis (pH 5.0, 4.5 and 4.0) and loss of sodium and chloride (pH 4.5 and 4.0) were moderate to severe. The acidosis at pH 5.0 and 4.5 was due to impaired aerobic respiration and therefore would have been more severe in active fish. At pH 4.0 aerobic respiration was not impaired, therefore the acidosis was probably due to influx of  $H^+$  from the environment.

In the control groups, at pH 6.1 and 5.0, ventilation, and blood and tissue chemistry were normal. At pH 4.5, coughing, slight acidosis and chloride loss occurred. At pH 4.0 impaired aerobic respiration caused a slight acidosis, but coughing and rate of sodium and chloride loss were much greater than in the experimental group and 91% of the fish died within three days. Thus the low level of aluminum deposited on the gills of the experimental fish at pH 4.0 appeared to afford a slight protection of ionoregulation in the gill epithelium from the high concentration of hydrogen ions. Gill histopathology is pending.

It is apparent that low levels of monomeric inorganic aluminum in the ambient water are toxic in a low pH environment between 6.1 and 4.5. The increased ventilation rate, impaired aerobic respiration and electrolyte loss will deplete the energy reserves of affected fish so that little energy will be available for foraging, growth, and gonad development. Such fish will also be highly susceptible to disease.

The second part of this study will deal with the effects of polymeric and organic monomeric species of aluminum combined with the toxic inorganic monomeric species. Such conditions are found in many of the dystrophic acidified lakes and streams. The combined information from both parts of this study will allow the response of fish to acidification in natural lakes and streams to be predicted much more easily and accurately than is now possible.

ALUMINIUM TRANSPORT IN ACIDIFIED STREAMS

DURING SPRING SNOWMELT

Ministry of the Environment Technology Transfer Conference No. 3

December 7, 1982 at the Constellation Hotel, Toronto, Ontario

Abstract for Paper No. B2

Introduction:

Bruce LaZerte

Aluminum has been identified as a major toxic substance in lakes and streams subject to increased levels of acidic precipitation (Dickson 1978; Baker and Schofield 1980; Grahn 1980; Muniz and Leivestad 1980; Driscoll et al 1980) and a causal relationship between high precipitation acidity and the leaching of aqueous aluminum from soils and streambeds has been demonstrated (Johnson *et al* 1981). In addition, spring snowmelt has been identified as a peak period of acid input to lakes and streams, as the winter accumulation of acidic pollutants in the snow pack is preferentially released at a faster rate than the snow melts (Johannessen and Henriksen 1978).

However, detailed knowledge of the effects of spring snowmelt on the aluminum levels of lakes and streams, and their potentially toxic effects are known for only one study in the Adirondacks (Driscoll 1980). This is primarily because the toxicity of aluminum is not directly related to the total, easily measured aluminum (e.g. Driscoll et al 1980) but primarily to the inorganic fraction, which is more difficult to measure. The organic complexes appear much less toxic (Driscoll et al 1980).

Consequently, the objectives of this research were to:

- i) develop an analytical method separating the inorganic aqueous species of aluminum (the potentially toxic forms) from the organic species (non-toxic) and to
- ii) examine the changes in the relative proportions of these forms from acidified headwater streams to the more neutralized locales such as downstream littoral zones and outflows, and to
- iii) determine the mechanisms responsible for these changes.

Site and Methods:

The site chosen for this study was the Plastic Lake watershed of the Muskoka-Haliburton area, Ontario. Specific sampling locations were chosen within the watershed and lake so that all major stream inputs were monitored, with particular emphasis on the single major inflow (site #1) as well as the outflow (#6) and five sites located in the littoral zone (#12-16). These last locations are potentially important to aquatic biota as spawning or feeding sites. In addition, a deep water station was monitored at four depths (1, 2, 5, and 10m) to determine any vertical patterns of inorganic aluminum (sites #23-26, respectively). All sampling was performed in the spring of 1982.

The separation of organic complexes of aluminum from the inorganic forms was by equilibrium dialysis (Truitt and Weber 1981; LaZerte, in prep.), followed by extraction of the aluminum from the dialysate with Oxine into MIBK (Barnes 1978). The Oxine extract was subsequently measured by GPAAS. Details of the methodology will be published elsewhere.

Stream discharge data was provided by Wolfgang Schieder, Ministry of the Environment, Rexdale, Ontario.

## Results and Discussion:

Discharge into Plastic Lake, from its major inflow, peaked around a 10 day period from 16 April to 26 April 1982 (Table 1). Ice break-up on the lake occurred just at the end of this peak flow period. The melt began, however, in Mid-March, with a small plateau of about 4 l/s until the beginning of April and then the subsequent rise to peak flow.

During this early stage of the melt, the inorganic aluminum fraction of the major inflowing stream (site #1) increased from approximately 45  $\mu\text{g/L}$  before March 10 to 90-100  $\mu\text{g/L}$  for the rest of March and the first half of April up until the 10 day peak flow period. A similar pattern was observed in the behaviour of littoral site #12, when after March 11, inorganic aluminum levels jumped from 5  $\mu\text{g/L}$  to 60  $\mu\text{g/L}$  and rose steadily to over 100  $\mu\text{g/L}$  until ice break-up. Littoral site #13 exhibited a more gradual rise of less magnitude than #12, eventually reaching 40  $\mu\text{g/L}$  of inorganic aluminum. Topographic analysis suggests that considerable amounts of soil throughflow discharges into the lake in the region of site #12, whereas the topography is less focused in the region of site #13.

At peak flow, the inorganic aluminum levels of the major inflowing stream peaked at 177  $\mu\text{g/L}$  (site #1) and then rapidly decayed as discharge dropped off. Throughout the melt, inorganic aluminum levels at littoral site #14 were relatively high (up to 100  $\mu\text{g/L}$ ) but extremely erratic. As this site was located only several meters offshore from site #1, the major inflow, it was surmised that the variability was the result of erratic stream discharge patterns under the ice.

By way of contrast, littoral sites 15 and 16 were located offshore of regions with little topographic concavity and were not close to any surface inflows. Here little ( $\leq 5 \mu\text{g/L}$ ) inorganic aluminum was observed until peak flow, at which time values of 60  $\mu\text{g/L}$  and 35  $\mu\text{g/L}$ , respectively, could be found. These patterns are similar to those observed at the lake outflow (#6) and the surface mid-lake station (#23) where peaks of 70  $\mu\text{g/L}$  and 40  $\mu\text{g/L}$ , respectively, were only obtained during peak flow, just before ice break-up.

During and after ice break-up, the whole lake turns over, dramatically diluting any aluminum inputs. Previously, flow directly under the ice predominates and the deeper layers with low inorganic aluminum concentrations ( $< 10 \mu\text{g/L}$ ) were short-circuited. During high periods of flow, the under-ice surface layers of the lake simply become a conduit for the massive amounts of stream and soilwater discharged into the lake and, consequently, high levels of inorganic aluminum can be flushed directly to the outflow with much less mixing and dilution than would normally occur. Following ice break-up and turn-over, inorganic aluminum levels throughout the lake and the outflow dropped to the low levels observed before spring melt (e.g. 26 April versus 3 March).



## Conclusions:

It has been demonstrated that, in this Southern Ontario watershed, spring snowmelt is associated with abnormally high levels of toxic inorganic aluminum in headwater streams, the littoral zone of headwater lakes and their outflows. The toxicity levels of the inorganic aluminum reported here relative to amphibian development, aquatic insect and fish survival has been studied simultaneously by teams of Ministry of the Environment scientists. Toxicity was demonstrated and will be reported in a separate publication.

## References:

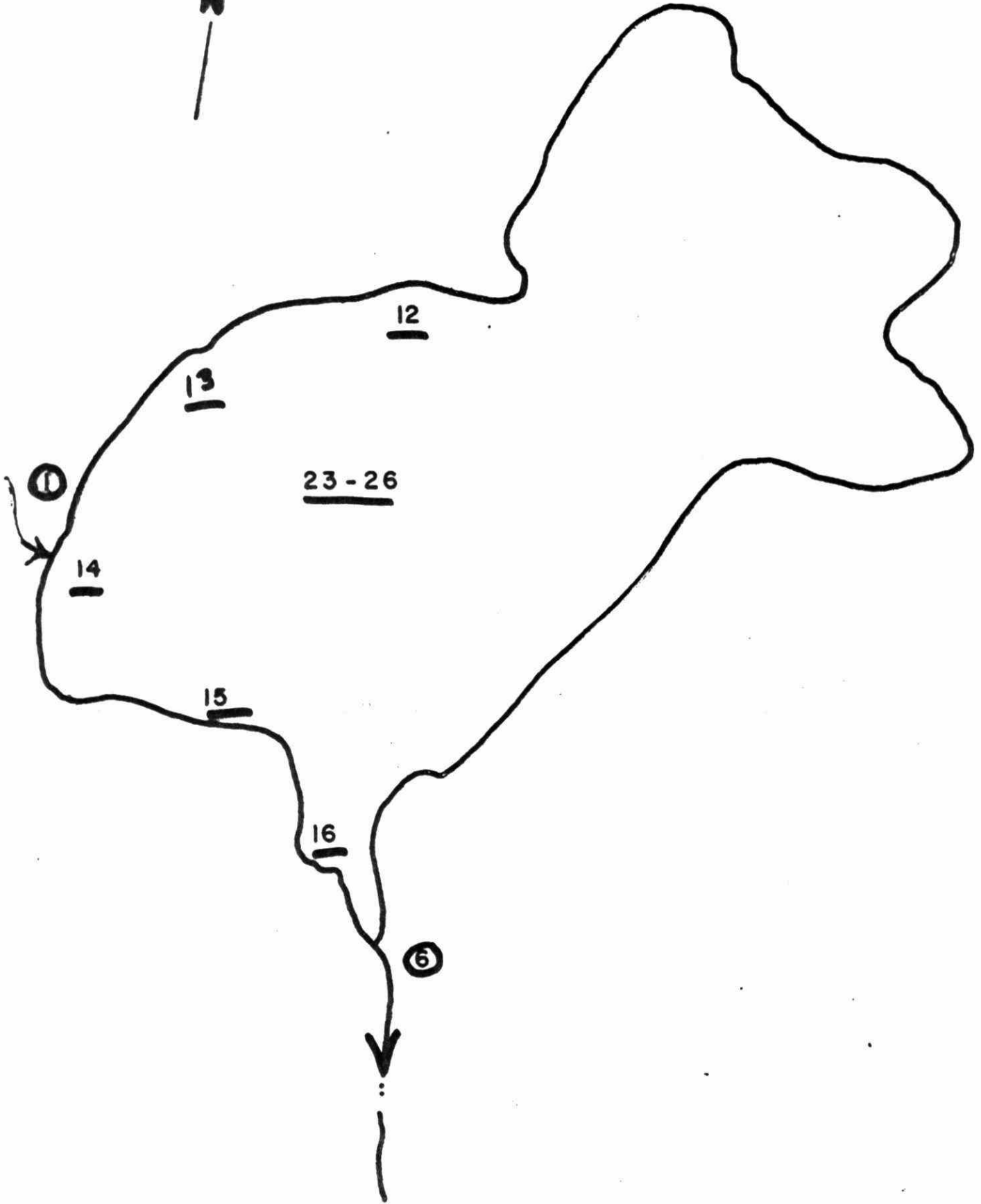
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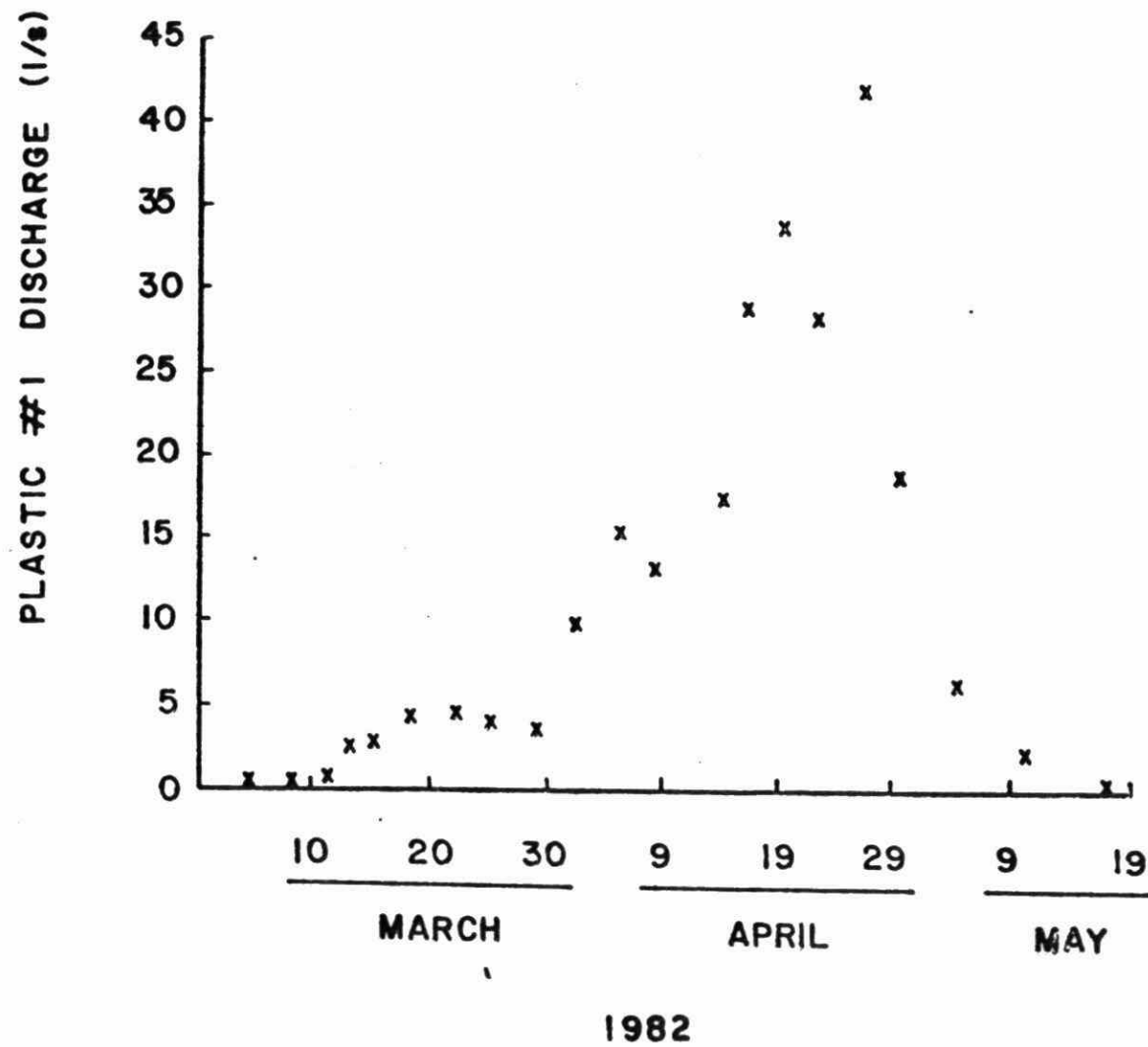


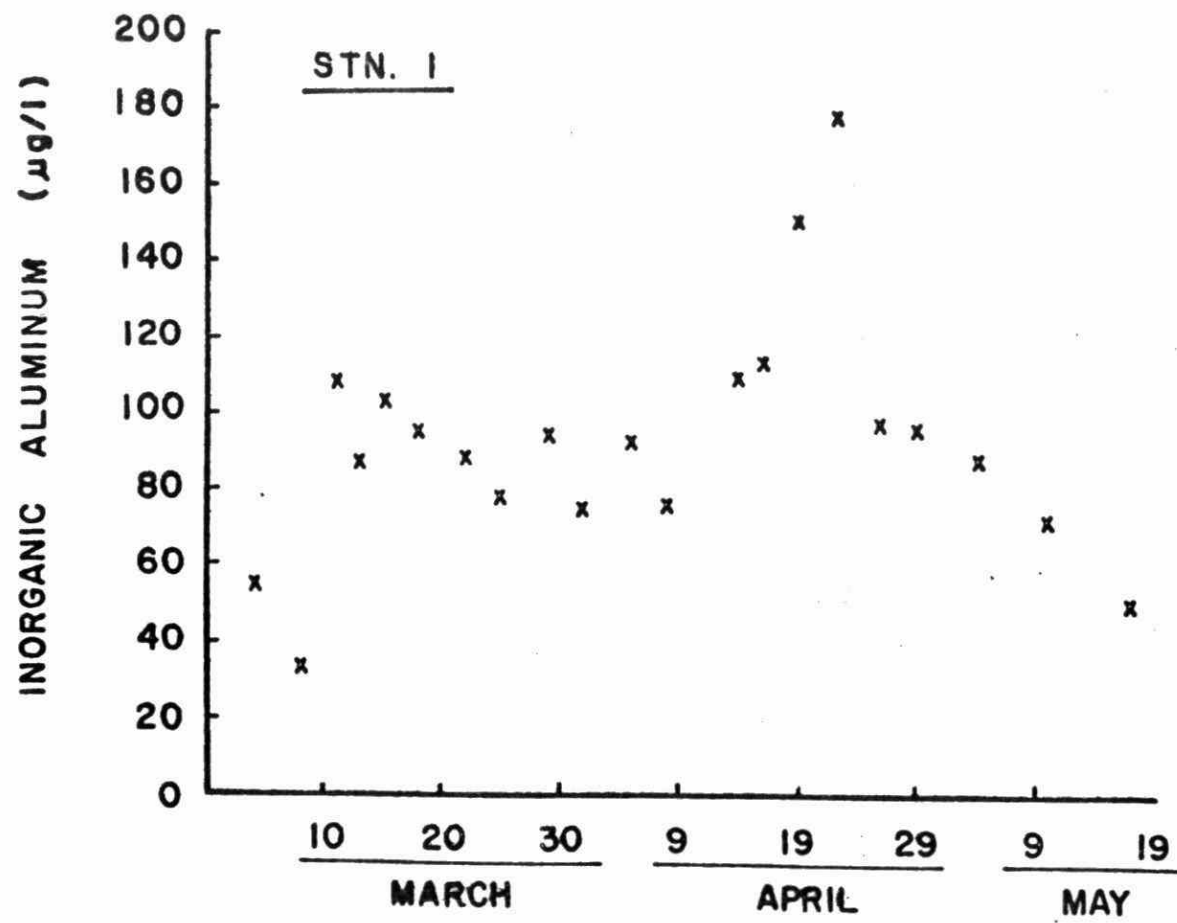
INORGANIC 1  $\mu$ g/L

<u>Date</u>													<u>Discharge</u> <u>1/s</u>
Day	Mo.	Stn 1	Stn 6	Stn 12	Stn 13	Stn 14	Stn 15	Stn 16	Stn 23	Stn 24	Stn 25	Stn 26	Stn 1
04	03	55	1	5	2	56	2	1	1	1	1	1	0.3
08	03	34	1	4	3	39	1	1	1	1	1	1	0.344
11	03	108	4	2	2	51	1	1	1	1	1	-	0.58
13	03	37	4	-	-	-	-	-	-	-	-	-	2.5
15	03	103	2	73	11	75	1	7	2	1	2	-	2.75
18	03	95	7	54	8	74	2	4	4	2	4	7	4.3
22	03	88	3	97	8	68	4	3	1	1	2	8	4.44
25	03	78	5	86	10	92	6	6	1	1	4	8	4.0
29	03	94	4	70	10	70	4	4	4	1	1	7	3.76
01	04	75	7	67	19	83	8	5	2	1	1	2	9.9
05	04	93	4	101	25	53	22	11	2	2	2	2	15.4
08	04	76	1	32	20	27	16	3	1	1	1	1	13.2
14	04	110	11	91	40	98	58	10	10	3	2	5	17.6
16	04	114	21	109	40	64	53	16	39	9	6	-	29
19	04	151	42	106	23	11	28	33	20	4	1	4	33.9
22	04	177	69	101	27	36	27	34	8	10	11	14	28.4
26	04	97	11	3	6	4	10	9	5	3	7	2	42.1
29	04	96	11	-	-	-	-	-	11	13	7	-	18.7
04	05	88	10	-	-	-	-	-	13	12	8	8	6.23
10	05	72	6	-	-	-	-	-	12	13	8	8	2.28
17	05	50	1	-	-	-	-	-	1	1	1	1	0.55

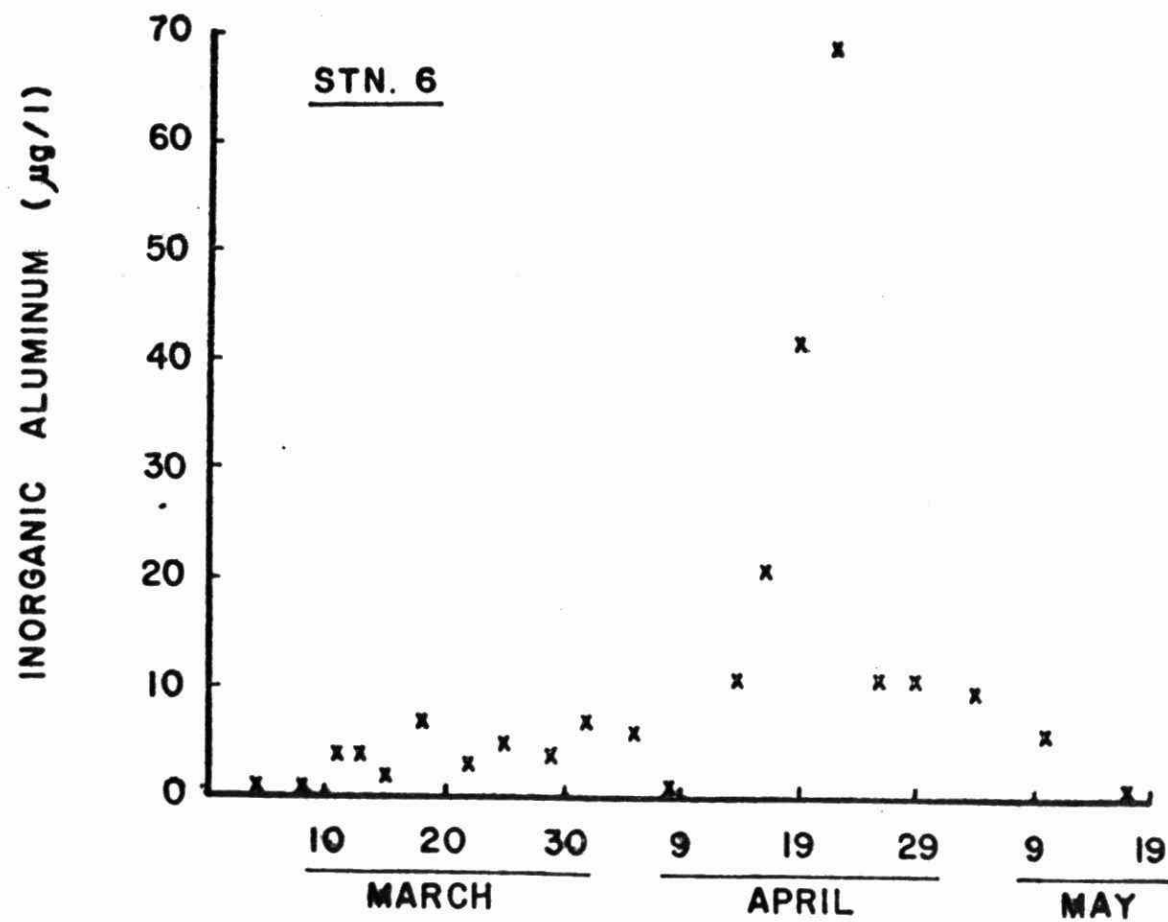
# PLASTIC LAKE



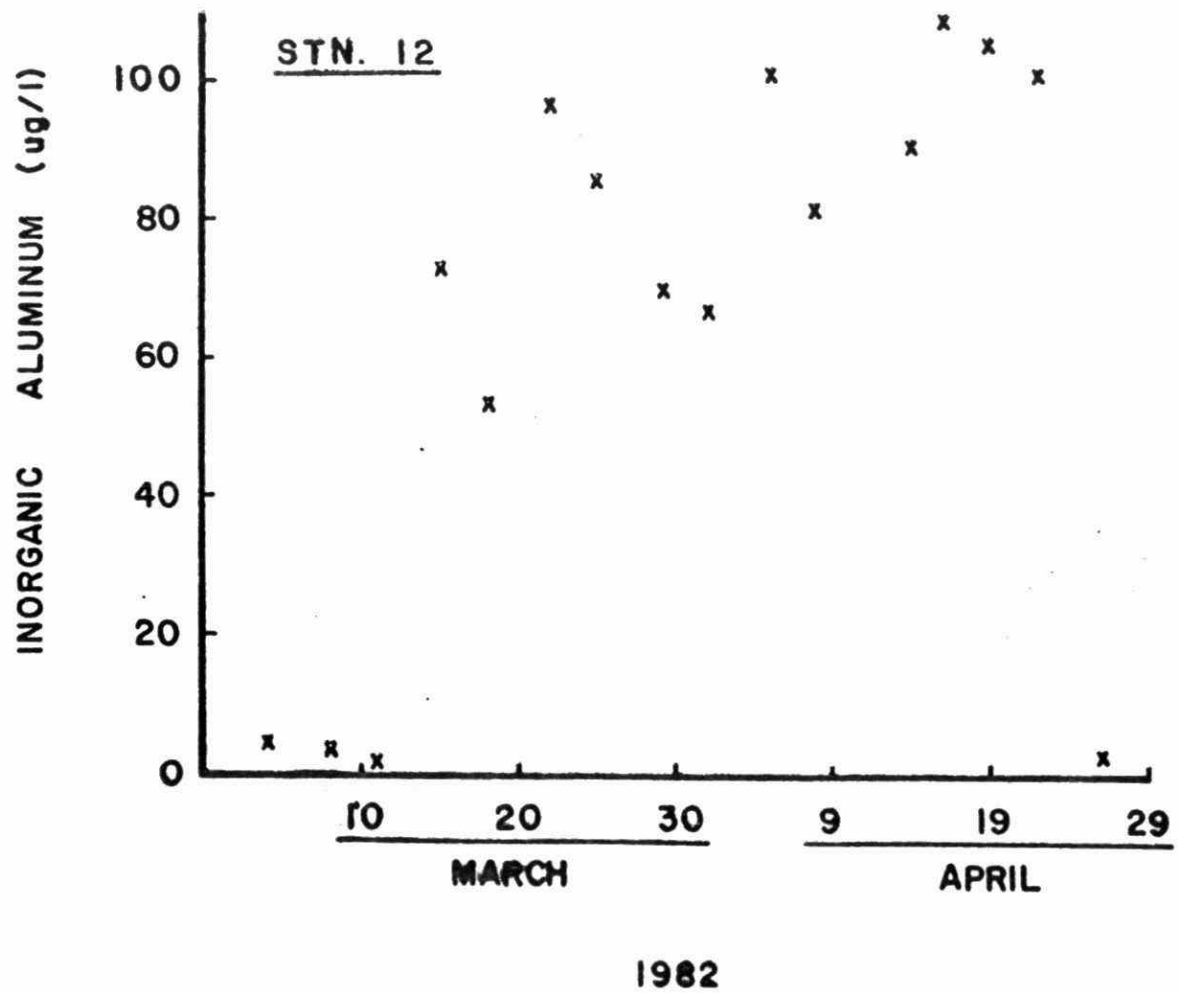


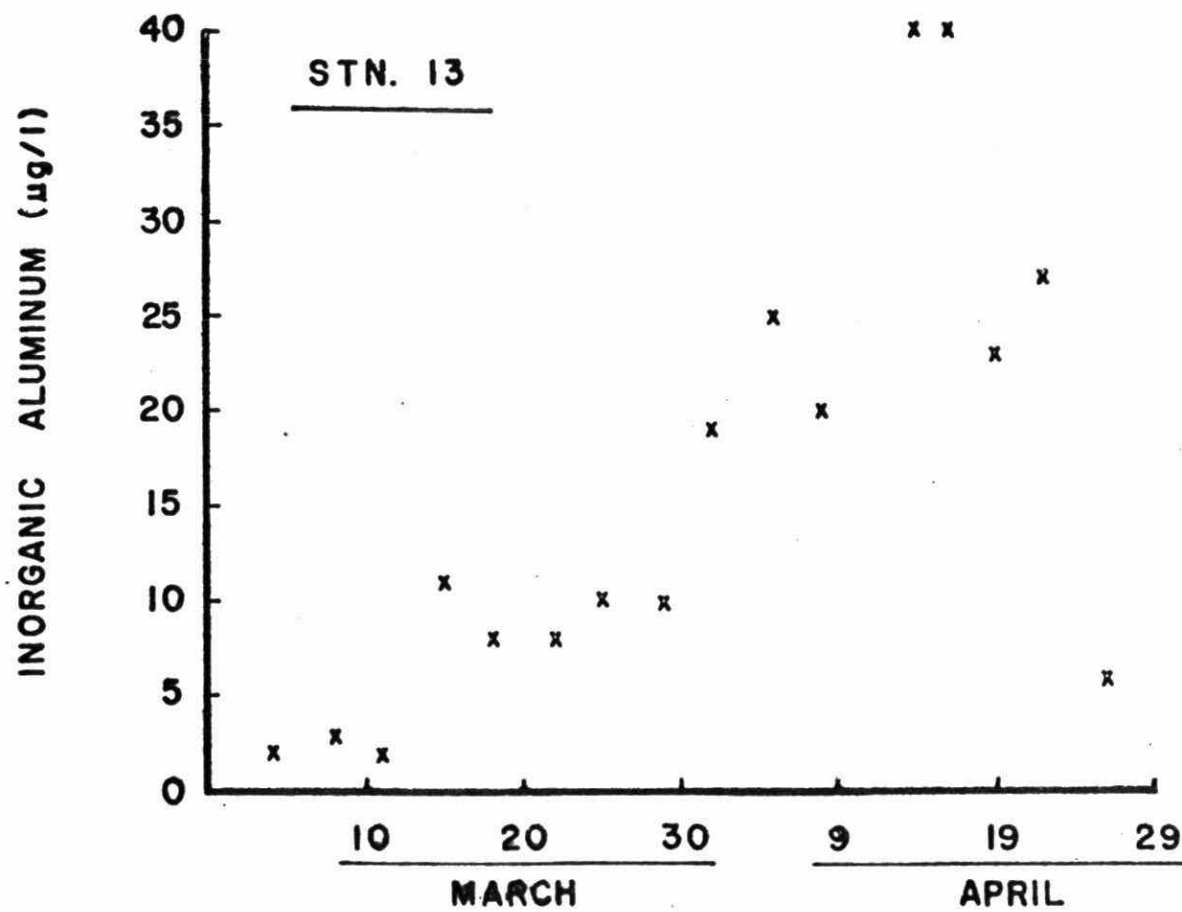


1982

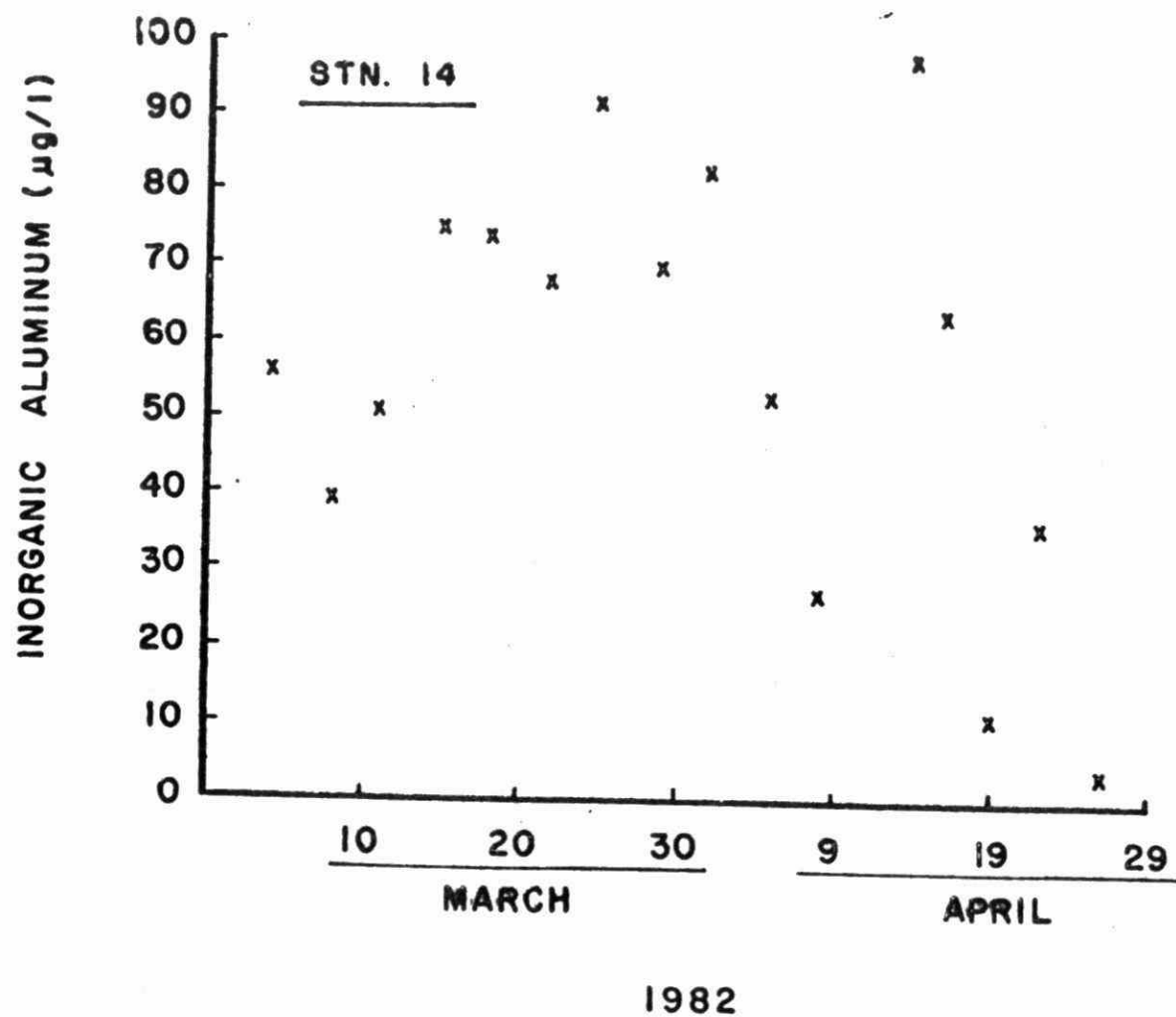


1982

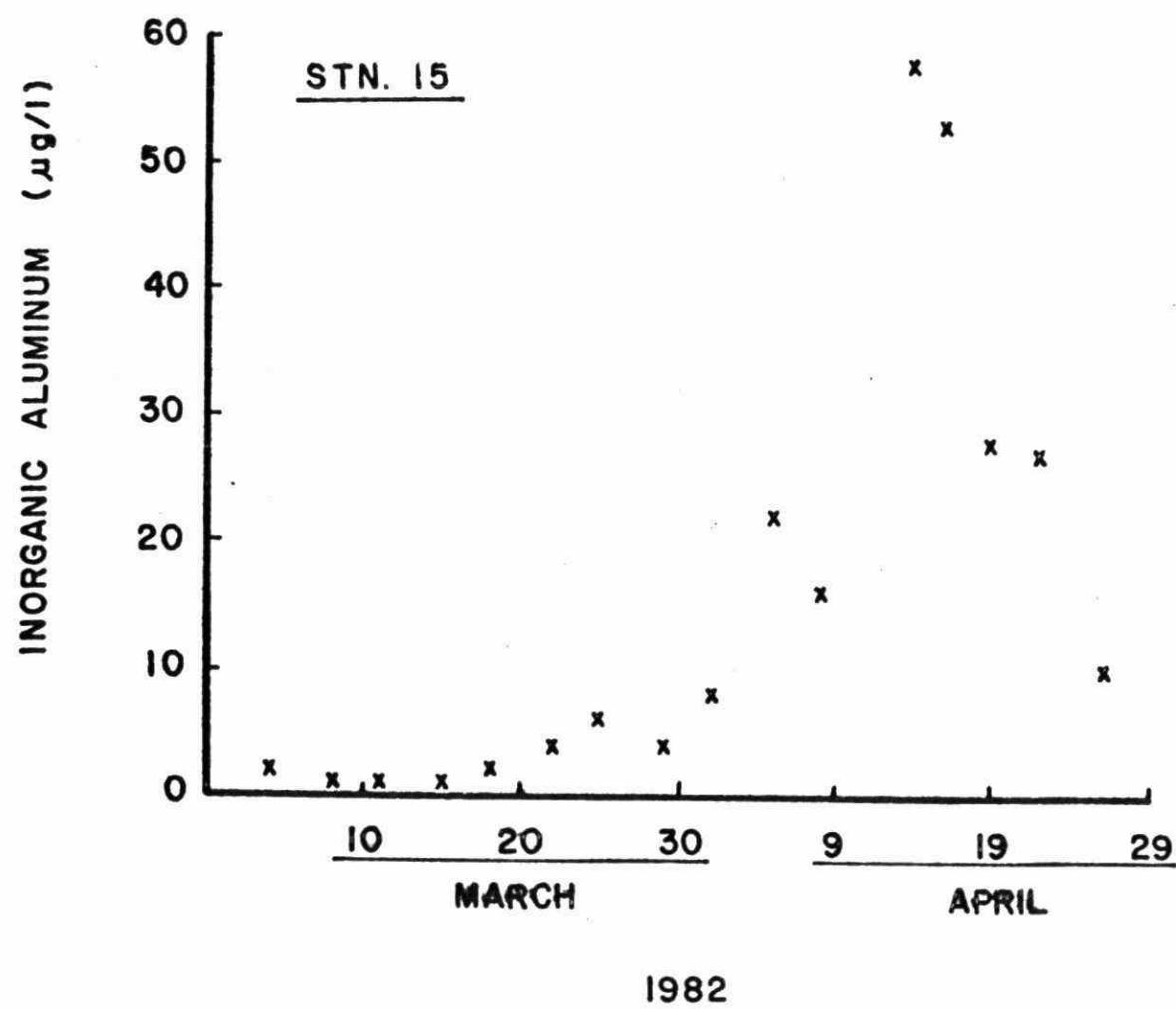


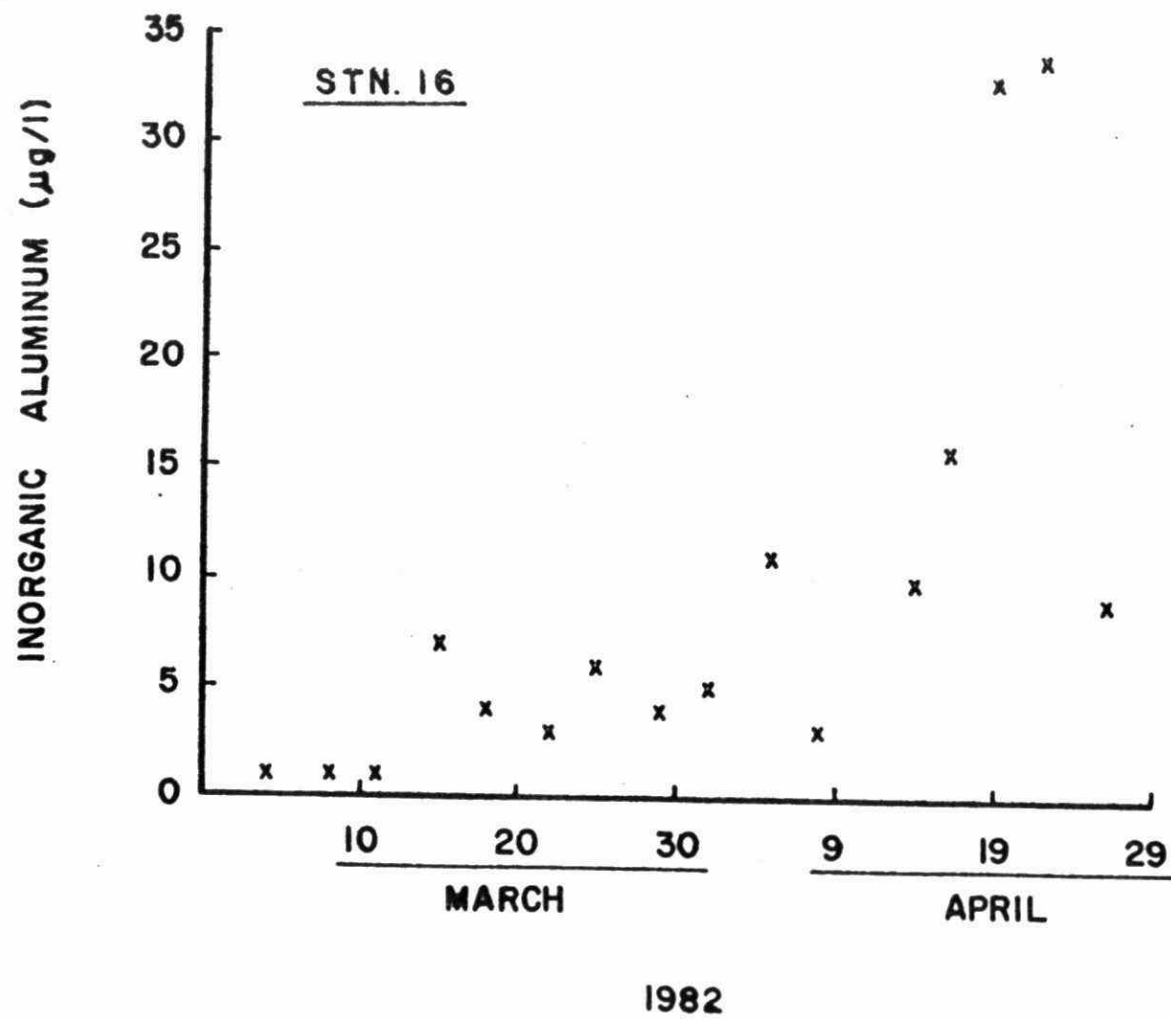


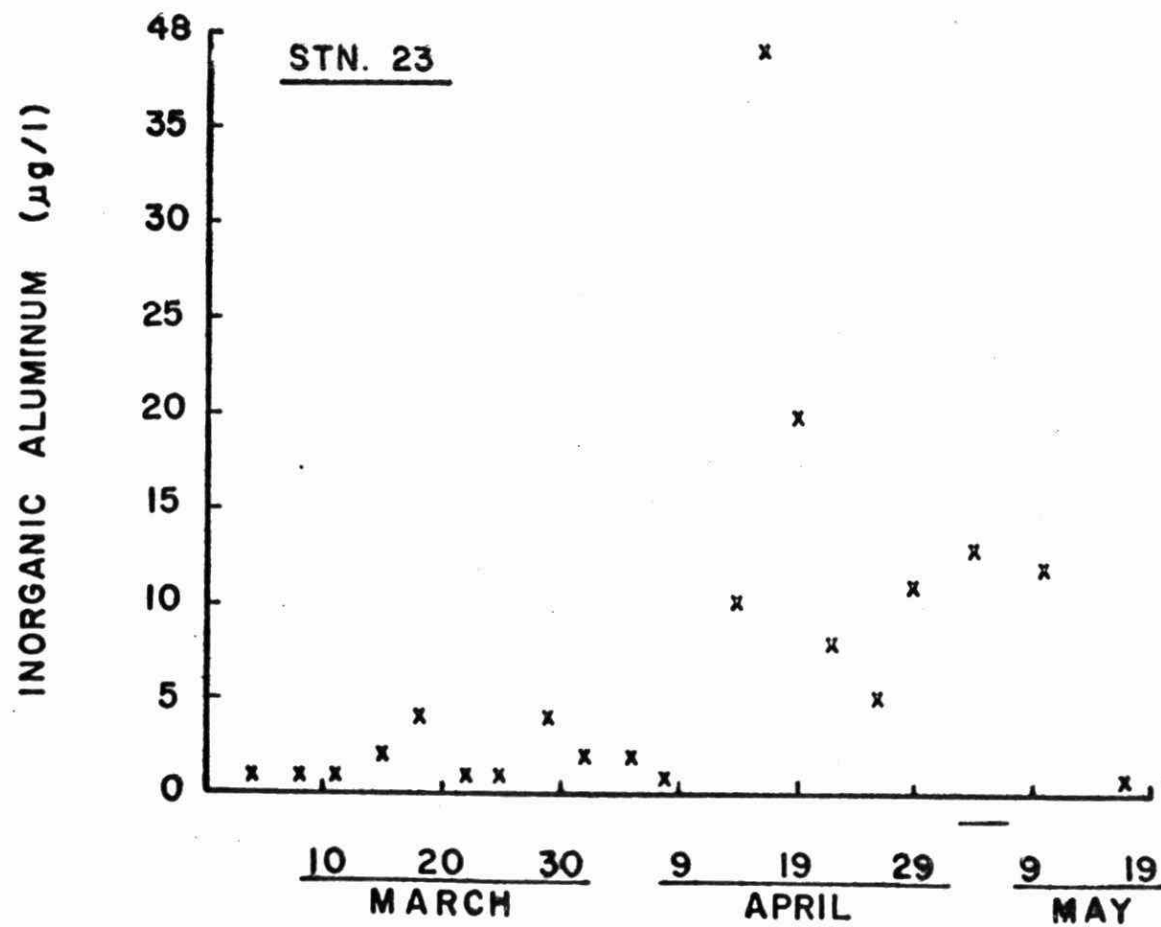
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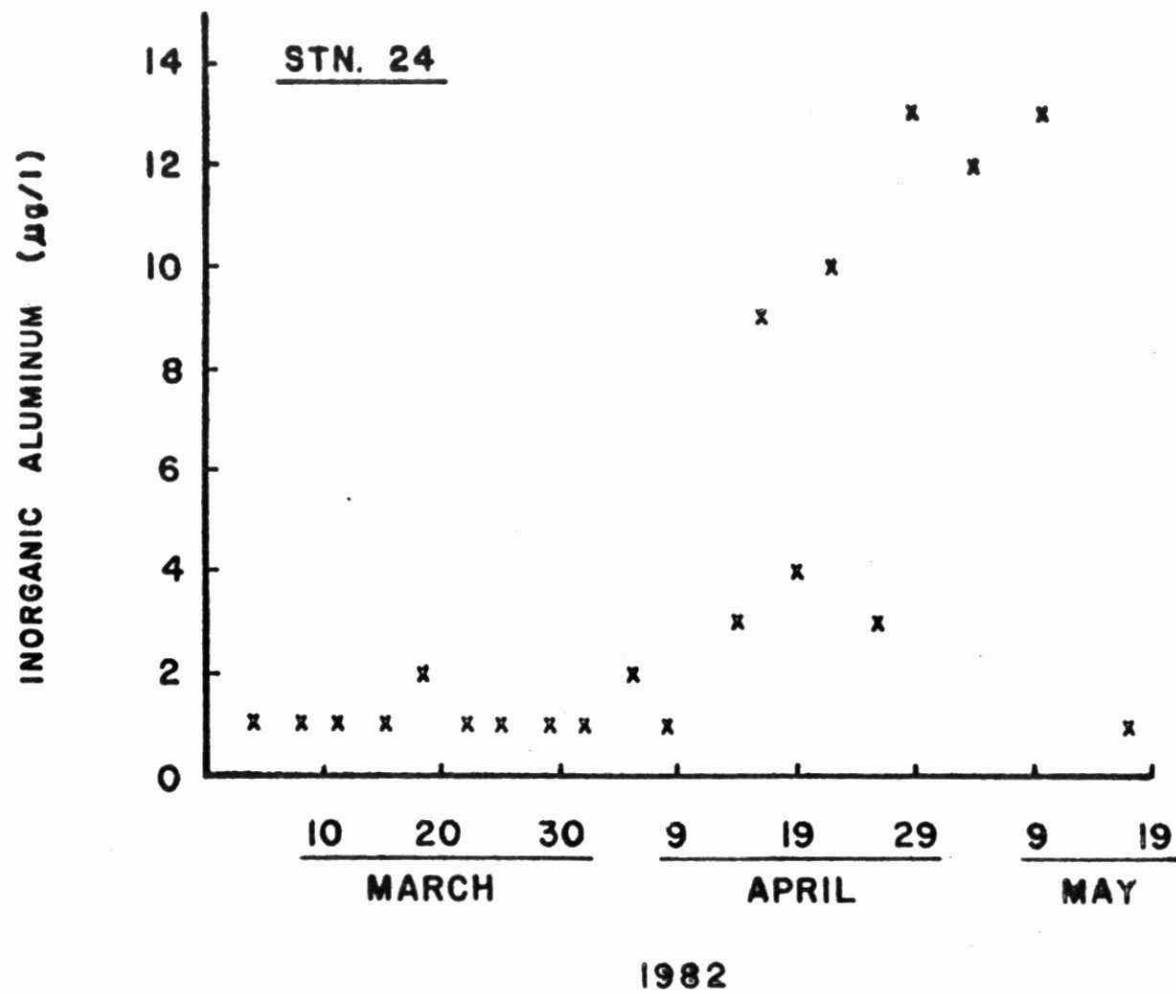


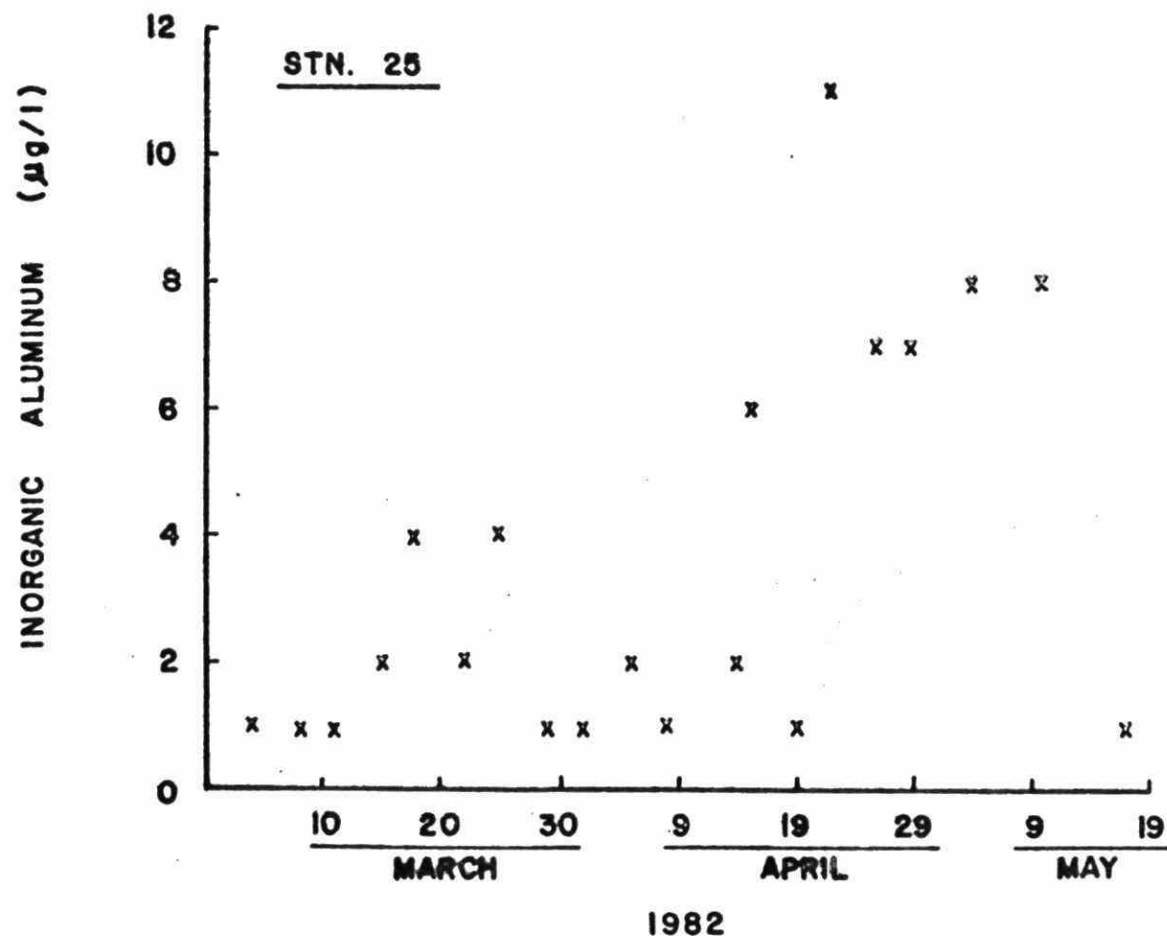




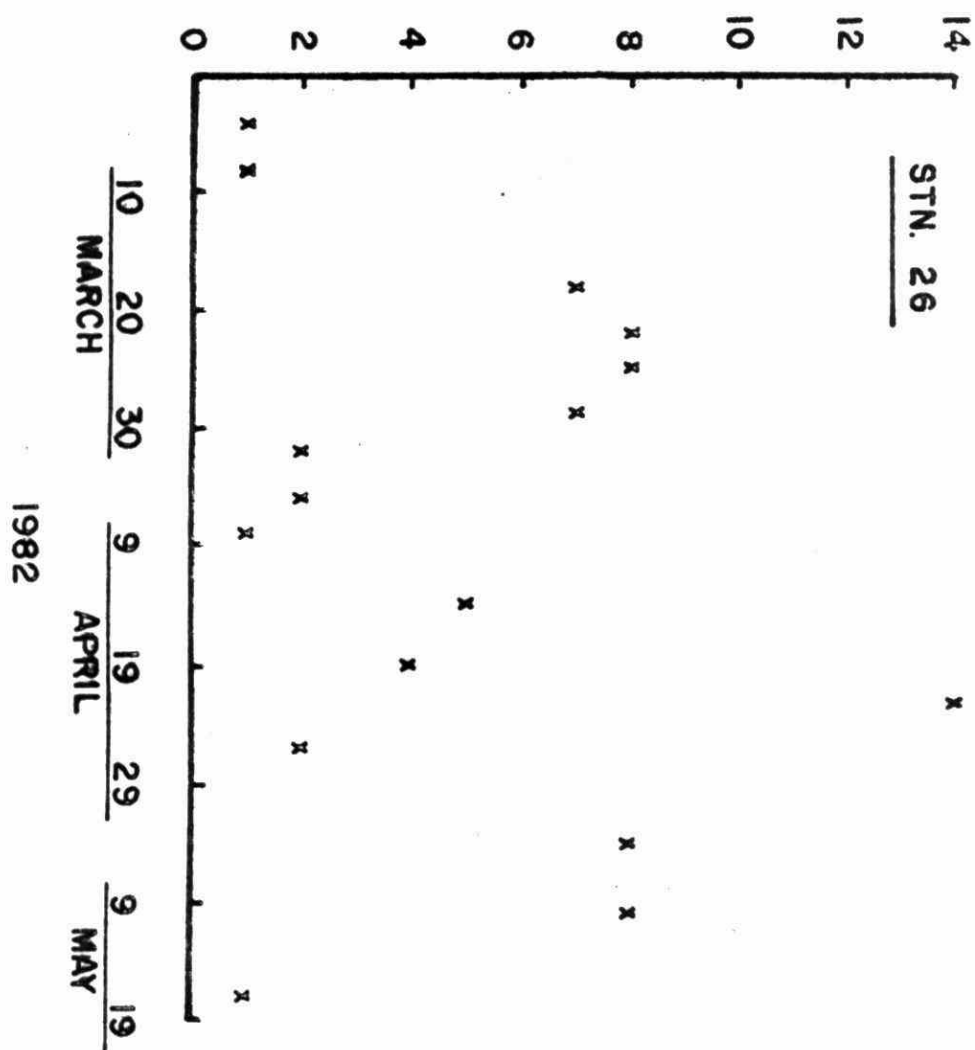


1982





# INORGANIC ALUMINUM ( $\mu\text{g/l}$ )



Aquatic Toxicity of Multiple Organic Compounds  
Chlorinated Benzenes

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and

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December 7, 1982.

# ABSTRACT

Results on the acute/chronic toxicity and bioconcentration in American flagfish of selected chlorinated benzenes (1, 4 - dichlorobenzene, 1, 2, 4 - trichlorobenzene and 1, 2, 4, 5 - tetrachlorobenzene) are presented.

The hypothesis that multiple toxicity is strictly dose-additive, at least within specific classes of chemical compounds, is applied in experimental designs and preliminary data analyses of acute and chronic flagfish toxicity tests conducted with mixtures of chlorobenzenes.

Bioconcentration dynamics in flagfish exposed to single chlorobenzene compounds and a triple chlorobenzene mixture are also discussed.



## Introduction

In 1978 the United States Environmental Protection Agency (EPA) published a list of 129 toxic chemicals for which industrial effluent limitations would be required. These toxic substances, commonly referred to as "priority pollutants", include 114 organic chemicals and 15 inorganic metals or ions (Keith and Telliard, 1979). Shortly after, Environment Canada developed a somewhat less extensive list of "priority chemical substances" for which regulations were being developed under the Environmental Contaminants Act (Brydon, 1978).

Over the past four years, many of these chemicals have been investigated in terms of their individual toxicity to aquatic organisms and, their potential to concentrate in biological tissues. A number of aquatic toxicity studies have also been conducted with various mixtures of the inorganic metals and/or ions on the priority pollutant list. However, very few studies with organic mixtures have been reported in the literature.

The U. S. EPA lists 21 point-source categories (classes of industrial effluents) which contain priority pollutants. Not surprisingly, most of these wastewaters are organic in substance, and always composed of two or more chemicals.

Hence, it is mixtures of toxic organic chemicals that are entering the water and sediments of the aquatic environment and it is the combined effects of these mixtures that require evaluation in terms of toxicity to and bioaccumulation in aquatic biota. Are the effects

of organic mixtures strictly additive or do they reflect more complex interactive processes such as inhibition or synergism? The answers to these questions will provide the necessary data base required by government agencies in the development of meaningful and scientifically sound regulations regarding industrial organic effluents.

Two groups of priority pollutants frequently identified in Ontario receiving waters adjacent to high density industrial areas are the chlorobenzenes and the chlorophenols. These compounds, therefore, are strong contenders as "Ontario priority pollutants" and provide a logical starting point to study the joint effects of organic chemicals on fish.

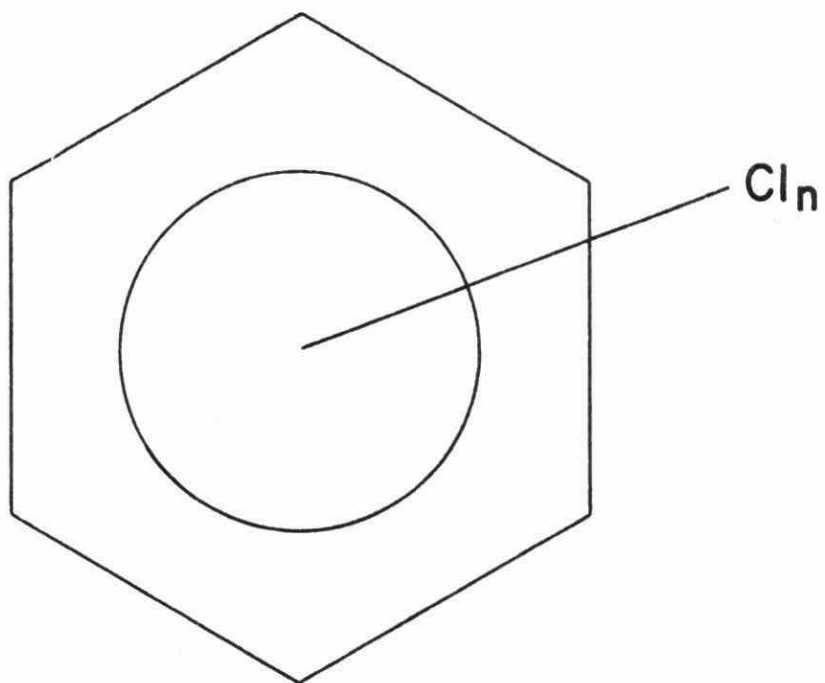
The aquatics research group at Lakehead University has recently completed the experimental work on chlorobenzenes and chlorobenzene mixtures and is now investigating the chlorophenols. The present address is a summary of the chlorobenzene studies.

#### The Chlorinated Benzenes

Chlorination of benzene yields 12 different compounds: mono-chlorobenzene, three isomers of dichlorobenzene, three trichlorobenzenes, three tetrachlorobenzenes, pentachlorobenzene and hexachlorobenzene. The structural formula for the chlorinated benzenes is illustrated in Figure 1.

Annual U. S. production figures during the early 1970's for

Fig. 01. Structural formula for chlorinated benzenes.



where  $n = 1, 2, 3, 4, 5, 6$ .

chlorobenzenes were approximately 139,000 kkg (metric tons) of monochlorobenzene, approximately 13,000 kkg of 1, 2, 4 - trichlorobenzene, approximately 8,000 kkg of 1, 2, 4, 5 - tetrachlorobenzene and approximately 300 kkg of hexachlorobenzene (West and Ware, 1977). The remaining chlorinated benzenes are produced mainly as by-products from the production processes for the preceding four chemicals (U. S. EPA, 1980).

Our studies concentrated on three specific chlorinated benzenes: 1) 1, 4, - dichlorobenzene; 2) 1, 2, 4 - trichlorobenzene; and, 3) 1, 2, 4, 5 - tetrachlorobenzene. The structural formulas for these compounds are presented in Figure 2. At room temperature, 1, 2, 4 - trichlorobenzene is a liquid, whereas 1, 4 - dichlorobenzene and 1, 2, 4, 5 - tetrachlorobenzene are solids.

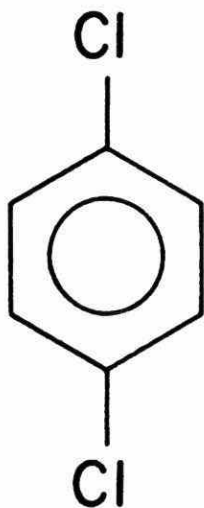
Criteria used in the selection of these specific isomers for study were primarily annual production figures and estimated quantities entering the environment yearly (U. S. EPA, 1980).

Monochlorobenzene is the major chemical in terms of production levels. But 70% of it is used as an intermediate in the synthesis of nitrochlorobenzenes, phenol and DDT (U. S. EPA, 1980). Hence, its primary use as a chemical intermediate limits its contamination of the aquatic environment to about 25% of its annual production.

Although 1, 4 - dichlorobenzene (1, 4 - DCB) is a by-product in the manufacture of monochlorobenzene, its annual production approaches 25,000 kkg (West and Ware, 1977). Its primary uses as an air deodorant and an insecticide results in the environmental release of essentially 100% of the production figure.

Fig. 02. Chlorobenzene compounds tested.

**1,4 - dichlorobenzene**

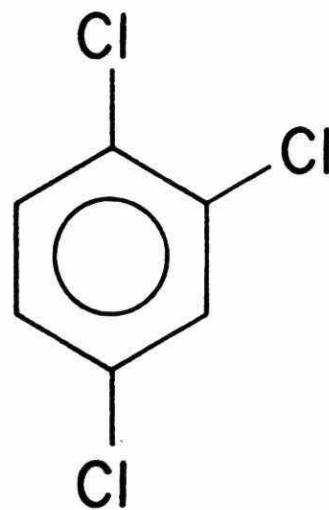


**1,4 - DCB**

**m.w. = 147.01**

**m.p. = 53 C**

**1,2,4 - trichlorobenzene**

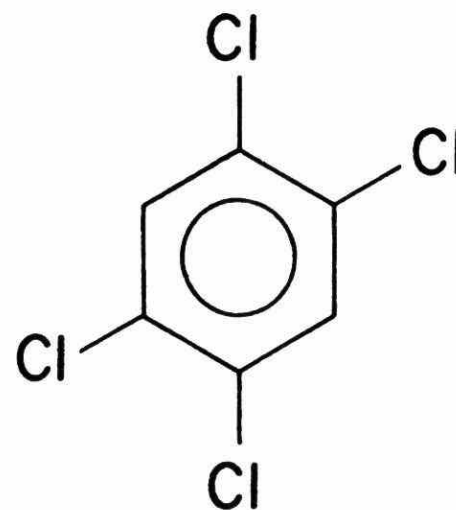


**1,2,4 - TCB**

**m.w. = 181.46**

**m.p. = 17 C**

**1,2,4,5 - tetrachlorobenzene**



**1,2,4,5 - TTCB**

**m.w. = 215.90**

**m.p. = 139 C**

About 46% of the 1, 2, 4 - trichlorobenzene (1, 2, 4 - TCB) produced is used as a dye carrier in the textile industry (U. S. EPA, 1980). It is also being increasingly used as a dielectric fluid in transformers to replace PCBs (Smith et al., 1980). It is estimated that more than 60% of the yearly production of 1, 2, 4 - TCB finds its way into the aquatic environment (U. S. EPA, 1980).

The only tetrachlorobenzene used in industrial applications is 1, 2, 4, 5 - tetrachlorobenzene (1, 2, 4, 5 - TTCB). Fifty-six per cent of the annual production of 1, 2, 4, 5 - TTCB is used in the production of the defoliant, 2, 4, 5 - trichlorophenoxy acetic acid, while another 11% is employed directly as a fungicide (U. S. EPA, 1980). Although the significance of environmental contamination by hexachlorobenzene is not intended to be under-rated, the annual production level for this chlorinated benzene is less than 4% that of 1, 2, 4, 5 - TTCB.

Pentachlorobenzene and the remaining isomers of dichloro-, trichloro- and tetrachloro- benzene have either no industrial significance or are used in more limited quantities as chemical intermediates in the manufacture of other organic compounds.

#### Protocol

##### 1. Water Supply.

The aquatics complex at Lakehead University receives its water from Lake Superior via the Thunder Bay municipal water system. Dechlorination is accomplished by routing the water through two 4,000-liter

charcoal/sand filter units. The water is periodically analyzed by the Chemical Laboratory Branch of the Ontario Ministry of the Environment (Northwestern Region) as part of our continuing water "quality control" program. Table 1 lists the physical/chemical characteristics of the Lake Superior water supply. All analyses are reported in mg/l (ppm) unless otherwise indicated.

## 2. Test Fish

The main portion of the chlorobenzenes study was conducted in our warm water laboratory utilizing the American flagfish, Jordanella floridae as the test organism. These fish are produced year round in our own culture facilities. Hence, flagfish from embryo to adult stages are always available for testing.

In our cold water laboratory we employed brook trout, Salvelinus fontinalis for partial chronic and bioconcentration testing with a single chlorinated benzene, 1, 2, 4, 5 - TTCB. The data collected from the trout experiments are not included in this presentation, but are available in an earlier report (Ozburn et. al., 1982).

## 3. Test Facilities

Toxicity and bioconcentration testing was conducted with flow-through apparatus which has been previously described (Smith et al., 1977).

Static tests utilizing 24-hour solution renewal were also employed to determine lethal concentration ranges prior to acute flow-through testing.

Table 1. Physical/chemical characteristics of the Lake Superior water supply\*

conductivity ( $\mu$ mhos/cm)	124.0
pH (pH units)	7.0
turbidity (Formazin units)	0.1
colour (Hazen units)	2.0
alkalinity as $\text{CaCO}_3$	33.0
hardness as $\text{CaCO}_3$	47.0
total phosphorus as P	0.002
dissolved reactive phosphorus as P	0.002
sulphate	10.0
chloride	3.8
ammonia nitrogen	0.02
Kjeldahl nitrogen	0.06
nitrite	<0.001
nitrate	0.25
iron	0.026
copper	0.05
nickel	0.006
lead	0.001
zinc	0.009
cadmium	0.001
chromium	0.013
free chlorine	not detectable
combined chlorine	not detectable

\* Analyses by the Chemical Laboratory Branch of the Ontario Ministry  
of the Environment.



#### 4. Carrier Material

Due to the hydrophobic nature of the chlorobenzenes, we used the solvent, acetone, as a carrier to introduce these chemicals into the diluter system. Acetone is relatively non-toxic, exhibiting a 96-hour  $LC_{50}$  to flagfish of 8500 mg/l (Ozburn et al., 1980). In the chlorobenzenes study, the concentration of acetone carrier did not exceed 3% of the  $LC_{50}$  value.

#### 5. Concentration Gradients

Nominal concentration gradients conformed with a recommended logarithmic series: 1.0, 1.8, 3.2, 5.6 and 10.0 (Sprague, 1973). The series is shifted up or down by a change in position of the decimal point.

#### 6. Analytical Chemistry

The determination of di, tri and tetrachlorobenzenes in water for toxicity testing was accomplished by solvent extraction with hexane and analysis by gas chromatography. Tissue analysis for bio-concentration testing involved digestion of the whole fish in methanolic NaOH, solvent extraction with hexane, Florisil cleanup of the extract, and concentration of the extract to a suitable volume using a Kuderna-Danish concentrator. The resulting extract was injected directly into the GC and analyzed using the same conditions as those employed for the water analyses. Specific details of the sampling and extraction procedures for water and tissue analyses are outlined in an earlier report (Ozburn et al., 1982). The GC conditions for measuring chlorinated benzenes are outlined in Table 2.

Table 02. Gas chromatographic analysis of chlorobenzenes.

Instrumentation: Hewlett-Packard GC system:  
(a) gas chromatograph, model #5730A  
(b) automatic sampler, model #7671A  
(c) sampler/event control module #19400A  
(d) integrator, model #3390A.

Column: 8% Bentone-34, 10% DC-200 on Gaschrom Q, 80-100 mesh.

Detector: ECD.

Detector Temperature: 300°C.

Injection Temperature: 150°C.

Oven Temperature: 130 - 150°C.

Carrier Gas: 5% methane/argon.

Carrier Gas Pressure: 50 psi.

Carrier Gas Flow: 50 ml/min.

Retention Times (130°):	1, 4 - dichlorobenzene	1.5 min.
	1, 2, 4 - trichlorobenzene	4.3 min.
	1, 2, 4, 5 - tetrachlorobenzene	8.2 min.
(150°):	1, 2, 4, 5 - tetrachlorobenzene	4.3 min.

The expression of bioconcentration parameters on a lipid weight basis involved the determination of flagfish total lipid content by the classical method of Bligh and Dyer (1959).

#### 7. Acute Testing

Ninety-six hour exposures at  $25 \pm 1^{\circ}\text{C}$  were conducted to generate  $\text{LC}_{50}$  values for 1, 4 - DCB, 1, 2, 4 - TCB, 1, 2, 4, 5 - TTCB and a triple mixture of these compounds. The acute tests employed both static and flow-through techniques. Both test procedures were conducted according to the methods described by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). The data reported for the static "rangefinder" tests are based on nominal (non-measured) chemical concentrations, whereas data generated by flow-through techniques utilized measured concentrations.

Both tests employed a duplicate 5- or 6-level concentration gradient. Duplicate water and acetone controls were always included. In the static tests, the number of juvenile (2 to 4 months) fish per test level was 10 (5 per duplicate). Twenty juveniles (10 per duplicate) were used in the flow-through tests conducted on individual chlorobenzenes. The triple mixture test used 10 fish in 4 test tanks (quadruplicates) at each exposure level.

Water samples from the flow-through tests were measured for chemical concentrations prior to introducing the fish and every 24 hours thereafter, throughout the 96-hour test. Thus, water sample size,  $N \geq 5$ . Measurements were conducted on both duplicates at each test level.

The concentrations of individual chlorinated benzenes were calculated by the standard mg/l (ppm) format. For the triple chlorobenzene mixture, mg/l units were converted to "acute toxic units" (a.t.u.'s).

by summing the ratios derived from the individual components of the mixture divided by their  $LC_{50}$  values.

Acute data was analyzed by computer, utilizing an  $LC_{50}$  program developed by Stephan (1977).

#### 8. Chronic Testing

Our "chronic" toxicity test for flagfish is similar to the early life stage (ELS) toxicity test developed for the fathead minnow, Pimephales promelas (Benoit et al., 1982).

Two age groups of flagfish were used in simultaneous flow-through exposures at  $25 \pm 1^{\circ}C$ : 1) embryo/larval fish, with data collected on hatching success and 10-day larval survival; and, 2) week old fry, with data generated on survival and growth over 28 days. The test gradients consisted of 5 duplicate concentrations with a duplicate water control. The 96-hour  $LC_{50}$ 's calculated from the acute data were used to establish the "sublethal" exposure gradients employed in the chronic tests conducted on individual chlorobenzenes (1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB).

Water samples from all exposure tanks were analyzed 5 days per week throughout the 28-day exposure periods. The fish were added after stable chemical concentrations were reached, which was usually 48 to 72 hours after dosing commenced.

The embryo/larval tests began with 50 fertilized eggs (25 per duplicate) at each test concentration and control. Eggs were  $\leq 24$  hours old. They were held in egg cups on a rocker arm assembly (Mount, 1968) during the incubation period (4 to 6 days). After hatching, the larvae

were transferred to fry retainers (Murphy, 1978) and held for a 10-day, post-hatch exposure period. Swim-ups were fed brine shrimp nauplii twice daily during the test. Observations on both egg and fish mortality were recorded daily. Fry retainers were cleaned daily to ensure a constant flow of water through them.

The 28-day survival and growth test commenced with 50 fry (one week old) per test level and control. Again, duplicate exposures were used, fish were fed twice daily with equal portions of brine shrimp nauplii, and observations on mortality were recorded daily.

The growth parameter was final weight after 28 days of exposure. The fish were terminated by overdosing with anesthetic (MS - 222), blotted dry, and wet weights determined to four decimal places. After weighing, the fish were preserved in Bouin's solution for possible future histological examination.

Several statistical procedures were used to evaluate the chronic data. The growth parameter (28-day weight) was tested for significance using one-way analysis of variance (ANOVA). If a significant F-ratio was found, a multiple range test (Duncan, 1955) was applied to determine which exposure levels were significantly different from control. Hatching success and survival parameters were analyzed using the Lee-Desu statistic (Lee and Desu, 1972), again, to determine which exposure levels differed significantly from control.

These statistical analyses allowed us to determine "estimated MATC's" for individual chlorobenzene compounds. Mount and Stephan (1967) define MATC (maximum acceptable toxicant concentration) as the hypothetical

toxic threshold concentration falling between the highest concentration showing no effect and the next higher toxicant concentration showing a significant toxic effect. The term "chronic value" is applied to this hypothetical toxic threshold concentration and is quantified as the geometric mean of the no effect/effect limits. Benoit et al. (1982) have qualified the MATC concept by prefixing the term "estimated" when applying it to ELS-type tests which expose discrete life stages for limited time periods in lieu of continuous exposure of all developmental stages which is standard methodology in a classical chronic test.

#### 9. Bioconcentration Testing

Bioconcentration testing of the chlorinated benzenes investigated was conducted according to the Proposed Standard Practice for Measuring Bioconcentration of Chemicals with Fishes (ASTM - Draft #8, 1978).

Juvenile flagfish (4 to 5 months old) were randomly distributed among 3 exposure tanks under flow-through conditions. Each tank received 48 fish. Flagfish in one set of duplicate tanks served as the exposed group, while those in the third, single tank were used as controls. Frozen adult brine shrimp was fed twice daily and tanks were siphoned once a day.

Test fish were exposed for a 28-day period to a nominal chemical concentration of 5  $\mu\text{g/l}$  (ppb) in 98 mg/l (100  $\mu\text{l/l}$ ) of acetone. During this "uptake" phase of the test, 6 exposed fish (3 per duplicate tank) and 3 control fish were sampled after 1, 3, 7, 14, 21 and 28 exposure days. Sacrificed fish were randomly selected, killed by immersion in ice water, placed in labelled plastic bags and kept frozen ( $-20^{\circ}\text{C}$ ) until analyzed for total chemical body burden.

The remaining test fish were transferred to a clean flow-through system for a 14-day depuration period. During this phase of the test, the same fish sampling procedure was followed after 1, 2, 3, 4, 5, 7, 10 and 14 days. Again, fish were randomly selected, killed by immersion in ice water and stored frozen in labelled plastic bags until analyzed.

During uptake, water samples were analyzed 5 days per week.

Data collected on water and tissue analyses were subjected to a computer program called Biofac. Developed by the Dow Chemical Company, Biofac has been documented by Blau and Agin (1978).

## Results and Discussion

### 1. Acute Toxicity

The nominal static tests performed on individual chlorobenzenes yielded  $LC_{50}$  values which agreed remarkably well with those reported in the literature for bluegill (Lepomis macrochirus) under similar test conditions (Table 3). The general trend of increasing toxicity with degree of chlorination is also readily apparent from the data in Table 3.

When these numbers were used in the triple mixture static to establish a nominal concentration gradient based on acute toxic units (a.t.u.'s), an  $LC_{50}$  value of 1.41 was generated (Table 4).

We have made the assumption that the toxicity of the components (1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB) in the mixture are strictly dose-additive. If this assumption is valid, 50% mortality should be equivalent to 1 a.t.u., but our triple mixture static yielded an  $LC_{50}$  of 1.41 a.t.u.'s. However, a non-measured static is a "fast and dirty"

Table 03. Nominal 96-hour  $LC_{50}$ 's for 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB to juvenile flagfish.<sup>a</sup>

Binomial Analysis

Chlorobenzene compound	$LC_{50}$ , mg/l.	
	Flagfish Value	Literature Value <sup>b</sup>
dichlorobenzene (1, 4 - DCB)	4.49	4.28
trichlorobenzene (1, 2, 4, - TCB)	3.99	3.36
tetrachlorobenzene (1, 2, 4, 5 - TTCB)	1.57	1.55

a) non-measured static tests with 24-hour solution renewal and acetone carrier at 196 mg/l.

b) bluegill, Lepomis macrochirus (U. S. EPA, 1978).



Table 04. Acute toxicity of a triple chlorobenzene mixture to juvenile flagfish.<sup>a</sup>

Test level	Concentration acute toxic units <sup>b</sup>	Number exposed	Per cent dead
0	0	10	0
1	0.25	10	0
2	0.5	10	0
3	1.0	10	0
4	2.0	10	100
5	4.0	10	100

Binomial Analysis

$$LC_{50} = 1.41 \text{ acute toxic units}$$

a) non-measured 96-hour static test with 24-hour solution renewal and acetone carrier at 196 mg/l.

b) 1 acute toxic unit = 1/3 of each of the static  $LC_{50}$  values for 1, 4 - DCB, 1, 2, 4 - TCB, and 1, 2, 4, 5 - TTCB in mg/l.

$$= 1/3 (4.49) + 1/3 (3.99) + 1/3 (1.57)$$

method, to be used only as a rangefinder test. With this in mind, the  $LC_{50}$  reported in Table 4 is close enough to unity to support the dose-additivity premise.

The chlorobenzenes, 1, 4 - DCB and 1, 2, 4 - TCB yielded smaller flow-through  $LC_{50}$  values than the static tests (Table 5). This is not unusual with flow-through testing of hydrophobic compounds like dichloro- and trichloro- benzenes which have relatively high vapour pressures, resulting in large evaporative losses from the system. Indeed, measured concentrations of 1, 4 - DCB and 1, 2, 4 - TCB were only 20 - 25% of nominal concentrations at most test levels.

The  $LC_{50}$ 's generated for 1, 4 - DCB and 1, 2, 4 - TCB are consistent with the trend of increasing toxicity with degree of chlorination. The apparent anomaly to this trend is 1, 2, 4, 5 - TTCB (Table 5). We would expect this compound to have the smallest  $LC_{50}$  value, not the largest. Furthermore, we would expect 1, 2, 4, 5 - TTCB to have a flow-through  $LC_{50}$  smaller than the static-generated value of 1.57 mg/l. These expected results would not be due to evaporative loss but rather, to the compound's low solubility in water. Indeed, solid lumps of 1, 2, 4, 5 - TTCB were readily visible in the diluter cells and exposure tanks during the acute flow-through test. Water samples taken during the test had to be filtered through a glass sinter to remove gross particles of chemical prior to solvent extraction and GC analysis. The  $LC_{50}$  of 2.15 mg/l for 1, 2, 4, 5 - TTCB presented in Table 5 therefore, may be artificially high due to an insoluble component still present in the water samples. To illustrate this point, we filtered the same water samples from the acute test through

Table 05. Measured 96-hour  $LC_{50}$ 's for 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB to juvenile flagfish.<sup>a</sup>

Binomial Analysis

<u>Chlorobenzene compound</u>	<u><math>LC_{50}</math>, mg/l.</u>
dichlorobenzene (1, 4 - DCB)	2.10
trichlorobenzene (1, 2, 4 - TCB)	1.29
tetrachlorobenzene (1, 2, 4, 5 - TTCB)	2.15

a) flow-through 96-hour tests with acetone carrier at 196 mg/l.

millipore filters of different pore size (Fig. 3). On the far right of this graph is the measured concentration gradient obtained with glass sintered samples (pore size  $\approx 50 \mu$ ). As the pore size of the filter decreases, the measured concentration of 1, 2, 4, 5 - TTCB also decreases. Extrapolation of these curves back to a pore size  $< 0.2 \mu$  results in measured concentrations of 1, 2, 4, 5 - TTCB all below 0.4 ppm (mg/l).

If we calculate  $LC_{50}$  values for each measured concentration gradient obtained with the millipore-filtered water samples we generate a series of  $LC_{50}$ 's all below 0.5 mg/l (Table 6).

The glass sinter sampling technique resulted in the highest measured concentration for 1, 2, 4, 5 - TTCB of about 2.5 mg/l. This value is roughly 5 times higher than the solubility of the compound in water. (We have determined the water solubility of 1, 2, 4, 5 - TTCB by several experimental methods. From our data, we estimate the solubility of the compound to be 0.4 to 0.5 mg/l). Table 6 indicates that the highest glass sintered value for 1, 2, 4, 5 - TTCB within our estimated solubility range for the compound is about 0.4 mg/l. However, no mortality was observed at this concentration (test level 2). Additional static tests conducted with saturated solutions of 1, 2, 4, 5 - TTCB produced no flagfish mortality after 10 days of exposure. We conclude, therefore, that 1, 2, 4, 5 - TTCB is not acutely toxic within 96 hours at water saturation. The observed acute toxicity of the compound in our flow-through test was a function of the particle size and distribution of the insoluble component to which the test organisms were exposed. We think that physical variations in test systems and variations in the chemical composition of diluent waters can affect the particle size

Fig. 03. Effects of filter pore size on measured concentrations of 1, 2, 4, 5 - tetrachlorobenzene.

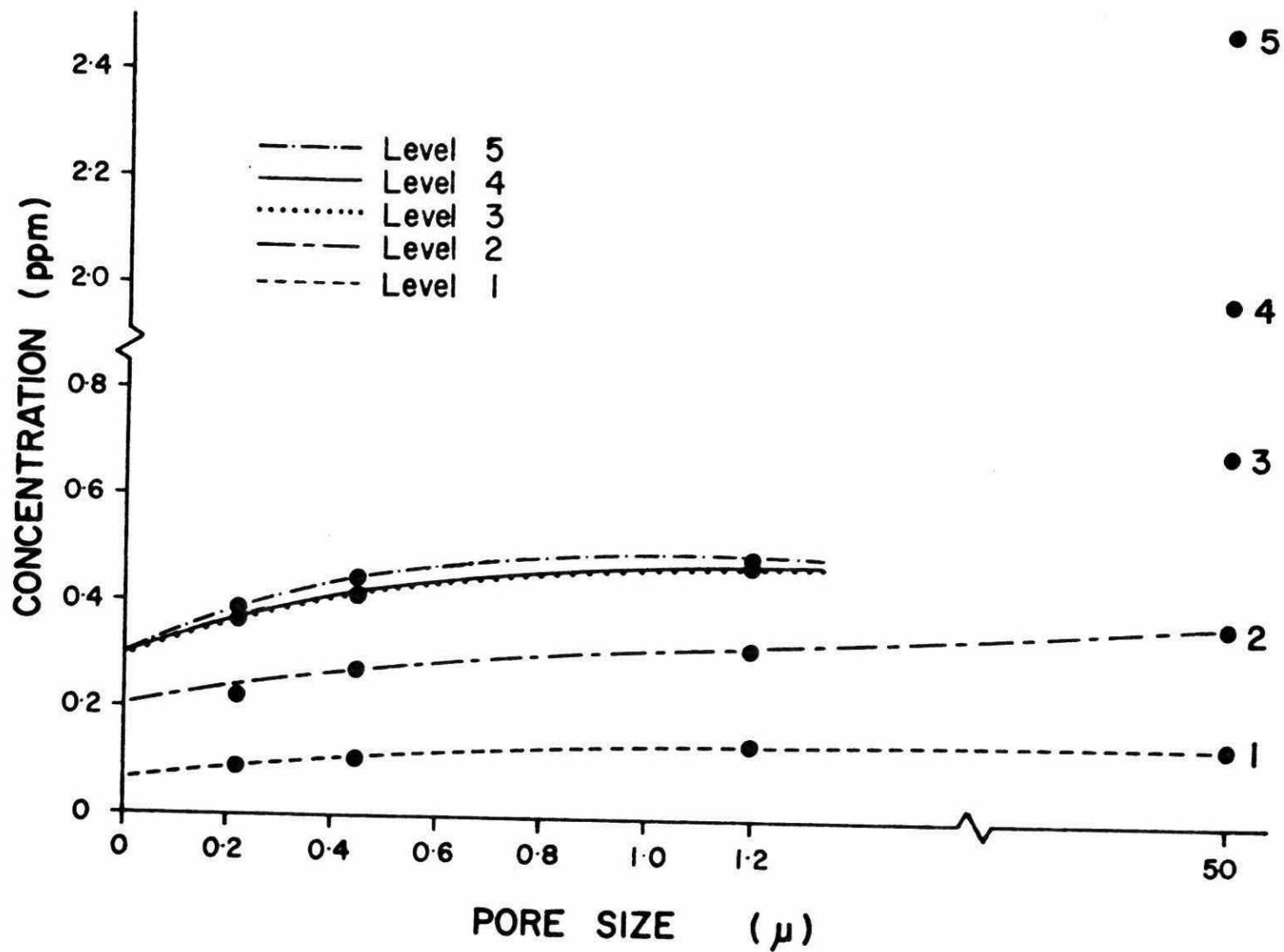


Table 06. LC<sub>50</sub> series for 1, 2, 4, 5 - tetrachlorobenzene by altering particle size/distribution of the non-soluble component.

Test level	Flagfish response # exposed      % dead		Concentration, mg/l of 1, 2, 4, 5 - tetrachlorobenzene ( $\bar{X} \pm S.D.$ )			
			Glass sintered 50 $\mu$	Filter pore size, $\mu$		
				1.2	0.45	0.22
1	20	0	0.148 $\pm$ 0.009	0.139 $\pm$ 0.009	0.108 $\pm$ 0.008	0.093 $\pm$ 0.005
2	20	0	0.363 $\pm$ 0.055	0.317 $\pm$ 0.061	0.274 $\pm$ 0.024	0.245 $\pm$ 0.040
3	20	20	0.695 $\pm$ 0.050	0.471 $\pm$ 0.033	0.412 $\pm$ 0.030	0.365 $\pm$ 0.025
4	20	35	1.855 $\pm$ 0.326	0.472 $\pm$ 0.046	0.417 $\pm$ 0.041	0.371 $\pm$ 0.035
5	20	65	2.493 $\pm$ 0.357	0.489 $\pm$ 0.009	0.447 $\pm$ 0.013	0.384 $\pm$ 0.025

#### Probit Analysis

LC <sub>50</sub> , mg/l	2.03	0.48	0.43	0.38
95% confidence limits	1.22 - 8.03	0.48 - 0.50	0.42 - 0.46	0.37 - 0.39
slope	2.56	63.21	31.10	54.82

and distribution of a hydrophobic chemical when dosing well above its true solubility. This may account for the often large differences in  $LC_{50}$  values for hydrophobic compounds like 1, 2, 4, 5 - TTCB that one finds in the published literature.

Once we had established flow-through  $LC_{50}$ 's for the individual chlorobenzene compounds, we conducted a triple mixture flow-through test. Again, the nominal dose gradient for the flow-through test was developed on the hypothesis that the toxicity of the mixture's components was dose-additive. Establishing a nominal concentration gradient for the stock solutions based on equal ratios of the components was straightforward; that is, 1 a.t.u. = 1/3 of each of the flow-through  $LC_{50}$  values of 1, 4 - DCB, 1, 2, 4 - TCB, and 1, 2, 4, 5 - TTCB in mg/l. However, due to physical variations in the diluter system (e.g., slight differences in flow-splitting) and variations in properties of the compounds (e.g., different vapour pressures and solubilities), it was not possible to maintain equal ratios for measured concentration values. Acute toxic units, therefore, were calculated on the basis of the relative contribution of each component using the formula:

$$\text{acute toxic units (a.t.u.'s)} = \sum_{i=1}^{i=n} \frac{\text{water concentration of } i}{\text{flow-through } LC_{50} \text{ value of } i}$$

where  $i$  = components in the mixture and

$n$  = number of components.

For our triple mixture test, the number ( $n$ ) of components ( $i$ ) was, of course, 3.

Quadruplicate test tanks at 5 levels of exposure yielded 20 sets of chemical analyses. It was possible to combine the chemistries for some of the individual tanks where each chlorobenzene component met the "1.2 ratio" criteria (Committee on Methods for Toxicity Tests with Aquatic Organisms, 1975). This enabled us to reduce the number of test levels to 9.

The calculated  $LC_{50}$  for the test was 1.34 a.t.u.'s (Table 7). Like the static test, this value is greater than the expected  $LC_{50}$  of 1 a.t.u. - if dose-additivity is a valid hypothesis.

We suspect that the tetrachlorobenzene component resulted in the  $LC_{50}$  value being greater than unity. Undissolved 1, 2, 4, 5 - TTCB was evident in all exposure tanks. This observation supported our earlier conclusion that the 2.15 mg/l  $LC_{50}$  value for the tetrachlorobenzene isomer was artificially high. If indeed this value was too high, then we had overweighted the toxic contribution of 1, 2, 4, 5 - TTCB in the mixture test. This appears to be the case. Dose-response curves constructed from data generated in the individual flow-through tests readily demonstrates why tetrachlorobenzene was a poor choice as the third component in the acute mixture test (Fig. 4). The odd-shaped curve obtained for 1, 2, 4, 5 - TTCB is due to the low solubility of the compound in water. Its toxic mode of action is completely different from that of 1, 4 - DCB and 1, 2, 4 - TCB which yield similar curves of the classical, sigmoidal shape.

We maintain that the dose-additivity concept is indeed valid for organic compounds of the same class which demonstrate similar modes of toxic action. If we remove the tetrachlorobenzene component and re-



Table 07. Acute toxicity of a triple chlorobenzene mixture to juvenile flagfish (Interim Table)<sup>a</sup>.

Test level	Concentration, acute toxic units <sup>b</sup>	Number exposed	Per cent dead
0	0	20	0
1	0.597	30	0
2	0.651	30	3.3
3	0.756	10	0
4	0.983	10	30
5	1.183	30	3.3
6	1.335	10	50
7	1.470	10	100
8	1.661	10	20
9	1.795	10	100

Binomial Analysis

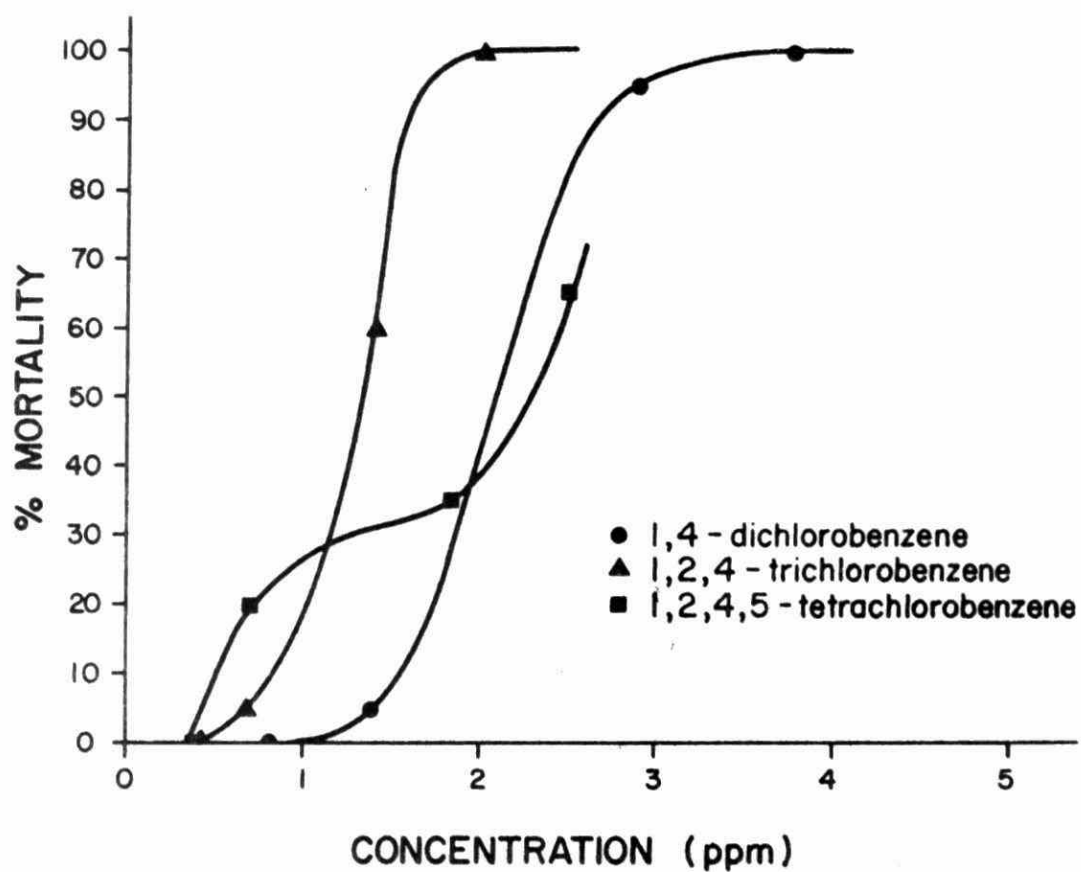
$$LC_{50} = 1.34$$

a) measured flow-through 96-hour test with acetone carrier at 196 mg/l.

b) acute toxic units (a.t.u.'s) = 
$$\sum_{i=1}^{i=n} \frac{\text{water concentration of } i}{LC_{50} \text{ of } i}$$

where n = 3 (1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB).

Fig. 04. Acute dose-response curves for 1, 4 - DCB, 1,2,4 - TCB and 1, 2, 4, 5 - TTCB.



process the acute mixture data using only di- and tri- chlorobenzene to calculate our concentration gradient, we can generate a 99%  $LC_{50}$  confidence interval of 0.78 to 1.36. This sufficiently encouraged us to recently run a flow-through binary acute test with 1, 4 - DCB and 1, 2, 4 - TCB. Preliminary analysis of the data indicates that we can readily bracket 1 a.t.u. Detailed results and discussion of the acute binary test will be available in a final report on the chlorobenzenes to be released at the end of this calendar year.

## 2. Chronic Toxicity.

Results of the ELS tests with 1, 4 - DCB indicate that exposure to a concentration range of 40 to 350  $\mu\text{g}/\text{l}$  had no effect on hatching success (Table 8, test 1) or 28-day survival and growth (Table 9). Ten-day larval survival, however, was significantly reduced at 325  $\mu\text{g}/\text{l}$  1, 4 - DCB (Table 8, test 1). In order to obtain an estimated MATC from which a chronic value could be calculated, we repeated the hatchability and 10-day larval tests at a higher concentration gradient. The estimated MATC for 1, 4 - DCB based on the larval survival parameter is 202 to 314  $\mu\text{g}/\text{l}$  (Table 8, test 2). The chronic value calculated from this interval is 252  $\mu\text{g}/\text{l}$ .

There were no chronic tests conducted with 1, 2, 4 - TCB. However, ELS data was previously collected by our research group on electrical grade trichlorobenzene (Smith *et al.*, 1979). Electrical grade TCB is an isomeric mixture of 1, 2, 4 - TCB ( $\approx 66\%$ ) and 1, 2, 3 - TCB ( $\approx 33\%$ ). Only the 10-day larval test was conducted by the same method as that

Table 08. Hatchability of embryos and 10-day larval survival for flagfish exposed to a concentration gradient of 1, 4, - dichlorobenzene.

1, 4 - dichlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ )						
Test I Parameter	0 $\pm$ 0 (control)	42 $\pm$ 7.1 (0.286 $\pm$ 0.048) <sup>a</sup>	93 $\pm$ 11.5 (0.633 $\pm$ 0.078)	111 $\pm$ 7.2 (0.755 $\pm$ 0.049)	230 $\pm$ 34.6 (1.565 $\pm$ 0.235)	325 $\pm$ 82.7 (2.211 $\pm$ 0.563)
Test level	0	1	2	3	4	5
hatchability, %	86	80	78	78	90	86
10-day survival, %	100	100	100	100	87	77 <sup>*</sup>

1, 4 - dichlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ )						
Test II Parameter	0 $\pm$ 0 (control)	124 $\pm$ 26.9 (0.843 $\pm$ 0.183)	202 $\pm$ 26.4 (1.374 $\pm$ 0.180)	314 $\pm$ 116.2 (2.136 $\pm$ 0.790)	620 $\pm$ 229.6 (4.218 $\pm$ 1.562)	835 $\pm$ 157.5 (5.680 $\pm$ 1.071)
Test level	0	1	2	3	4	5
hatchability, %	90	82	92	86	82	82
10-day survival, %	98	100	83	74 <sup>*</sup>	78 <sup>*</sup>	67 <sup>*</sup>

#### Lee-Desu Analysis

hatchability: Test I and Test II - not significantly different from control.

10-day survival: Test I - test level 5 (\*) significantly different from control ( $P < .01$ )

Test II - test levels 3, 4, and 5 (\*) significantly different from control ( $P < .01$ )

a) numbers in brackets denote concentrations in  $\mu\text{mol/l}$ .

Table 09. Survival and weight of week old flagfish exposed for 28 days to a concentration gradient of 1, 4 - dichlorobenzene.

Parameter	1, 4 - dichlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ )					
	0 $\pm$ 0 (control)	44 $\pm$ 7.2 (0.299 $\pm$ 0.049) <sup>a</sup>	91 $\pm$ 11.3 (0.619 $\pm$ 0.077)	111 $\pm$ 8.1 (0.755 $\pm$ 0.055)	229 $\pm$ 32.2 (1.56 $\pm$ 0.219)	349 $\pm$ 76.7 (2.37 $\pm$ 0.52)
Test level	0	1	2	3	4	5
28-day survival, %	100	100	100	98	100	98
weight, mg ( $\bar{X} \pm S.D.$ )	50 $\pm$ 19	53 $\pm$ 18	51 $\pm$ 15	53 $\pm$ 22	47 $\pm$ 16	51 $\pm$ 15

#### Lee-Desu Analysis

28-day survival - not significantly different from control.

#### Anova/Duncan Analysis

growth - not significantly different from control.

a) numbers in brackets denote concentrations in  $\mu\text{mol/l}$ .

employed in the ELS tests with the dichlorobenzene and tetrachlorobenzene compounds. The estimated MATC for electrical grade TCB based on 10-day survival of flagfish larvae is 910 to 1410  $\mu\text{g/l}$  (Table 10). This interval yields a chronic value of 1133  $\mu\text{g/l}$ .

ELS tests conducted with 1, 2, 4, 5 - TTCB produced no effect on hatchability or larval survival at concentrations up to and including 238  $\mu\text{g/l}$  (Table 11). However, the exposure of week old flagfish fry to a similar concentration gradient of 1, 2, 4, 5 - TTCB for 28 days did result in significant reductions in survival at 182  $\mu\text{g/l}$  and growth at 104  $\mu\text{g/l}$  (Table 12).

The estimated MATC for flagfish exposed to 1, 2, 4, 5 - TTCB is 69 to 104  $\mu\text{g/l}$  (chronic value, 85  $\mu\text{g/l}$ ), based on fry growth. Fry survival over 28 days was less sensitive, with a chronic value of 138  $\mu\text{g/l}$  (estimated MATC, 104 to 182  $\mu\text{g/l}$ ). Hatching and larval survival were the least sensitive parameters ( $> 238 \mu\text{g/l}$ ).

Chronic toxicity of the chlorinated benzenes should parallel that of acute toxicity; that is, if acute toxicity is dose-additive, then chronic toxicity should also be dose-additive.

Using our estimated MATC's and those available in the literature (U. S. EPA, 1980), we established a triple mixture concentration gradient composed of 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB which spanned no effect/effect levels for each component. ELS tests were then conducted using this concentration gradient. The data from these tests are still undergoing analysis but preliminary results are presented here in the form of Interim Tables.

Table 10. Ten-day survival of flagfish larvae exposed to a concentration gradient of electrical grade trichlorobenzene<sup>a</sup>.

Parameter	Electrical grade trichlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ ) <sup>b</sup>			
	Control	910 $\pm$ 130	1410 $\pm$ 160	2810 $\pm$ 90
Test level	0	1	2	3
10-day survival, %	93	98	59*	1*

Lee-Desu Analysis

10-day survival - test levels 2 and 3 (\*) significantly different from control ( $P < .01$ ).

a) data from Smith et al., 1979

b) an isomeric mixture of 1, 2, 4 - TCB ( $\approx 66\%$ ) and 1, 2, 3 - TCB ( $\approx 33\%$ )

Table 11. Hatchability of embryos and 10-day survival of flagfish larvae exposed to a concentration gradient of 1, 2, 4, 5 - tetrachlorobenzene.

Parameter	1, 2, 4, 5 - tetrachlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ )					
	0±0 (control)	36±4.0 (0.167±0.019) <sup>a</sup>	71±12.4 (0.329±0.057)	105±13.8 (0.486±0.064)	185±26.3 (0.857±0.122)	238±54.4 (1.102±0.252)
Test level	0	1	2	3	4	5
hatchability, %	88	84	86	76	88	82
10-day survival, %	100	100	100	100	100	100

Lee-Desu Analysis

hatchability - not significantly different from control

10-day survival - not significantly different from control

a) numbers in brackets denote concentrations in  $\mu\text{mol/l}$ .



Table 12. Survival and weight of week old flagfish exposed for 28 days to a concentration gradient of 1, 2, 4, 5 - tetrachlorobenzene.

Parameter	1, 2, 4, 5 - tetrachlorobenzene, $\bar{X} \pm S. D.$ ( $\mu\text{g/l}$ )					
	0±0 (control)	36±3.5 (0.167±0.016) <sup>a</sup>	69±10.2 (0.320±0.047)	104±11.5 (0.482±0.053)	182±24.5 (0.843±0.113)	251±50.3 (1.163±0.233)
Test level	0	1	2	3	4	5
28-day survival, %	96	82	98	88	74 <sup>*</sup>	70 <sup>*</sup>
weight, mg ( $\bar{X} \pm S.D.$ )	50±22	55±21	45±18	40±12 <sup>*</sup>	42±14 <sup>*</sup>	42±12 <sup>*</sup>

Lee-Desu Analysis

28-day survival - test levels 4 and 5 (\*) significantly different from control ( $P < .01$ )

Anova-Duncan Analysis

growth - test levels 3, 4, and 5 (\*) significantly different from control ( $P < .01$ )

a) numbers in brackets denote concentrations in  $\mu\text{mol/l}$ .

As expected, the triple chlorobenzene mixture did not affect hatching success (Table 13). As a general rule, fish embryos tend to be fairly resistant to toxic organic chemicals. For example, as shown earlier in this presentation, independent tests with the DCB and TTCB compounds did not produce significant effects on the hatchability parameter. Furthermore, concentrations in excess of 2000 µg/l of electrical grade TCB were required to reduce hatching success in flagfish embryos (Smith et al., 1979).

Ten-day survival of flagfish larvae was significantly affected by the triple chlorobenzene mixture (Table 14), as well as 28-day fry survival and growth (Table 15).

The exciting aspect of the data in Tables 14 and 15 is that all three parameters span the no effect/effect exposure levels, which will enable us to determine estimated MATC's and calculate chronic values. The general idea is to use the estimated MATC's and chronic values determined on individual compounds to convert the concentrations of the mixture's components to chronic toxic units (c.t.u.'s). By using a combination of our own data and available literature data, we hope to demonstrate that the chronic toxicity of multiple chlorinated benzenes is strictly additive. There are only 2 or 3 published papers in the world that have attempted to experimentally validate this concept of chronic dose-additivity.

In the event that the triple chlorobenzene mixture proves too complex to handle because the hydrophobic tetrachlorobenzene component

Table 13. Hatchability of flagfish embryos exposed to a triple chlorobenzene mixture (Interim Table).

Parameter	Test level					
	0 (control)	1	2	3	4	5
chlorobenzenes, $\bar{X} \pm S. D. (\mu g/l):$						
1, 4 - DCB	0±0	76±2.0	164±8.0	249±14.1	523±18.9	879±43.6
1, 2, 4 - TCB	0±0	81±2.6	168±7.9	256±13.0	527±17.7	810±38.9
1, 2, 4, 5 - TTCB	0±0	47±1.3	96±3.6	153±7.4	296±5.0	346±42.0
hatchability, %	98	90	90	100	96	94

Lee-Desu Analysis

hatchability - not significantly different from control.

Table 14. Ten-day survival of flagfish larvae exposed to a triple chlorobenzene mixture (Interim Table).

Parameter	Test level					
	0 (control)	1	2	3	4	5
chlorobenzenes, $\bar{X} \pm S. D. (\mu g/l)$						
1, 4 - DCB	0 $\pm$ 0	78 $\pm$ 4.2	185 $\pm$ 12.3	292 $\pm$ 28.6	514 $\pm$ 58.4	776 $\pm$ 128.8
1, 2, 4 - TCB	0 $\pm$ 0	82 $\pm$ 4.0	188 $\pm$ 12.1	296 $\pm$ 26.8	507 $\pm$ 48.4	726 $\pm$ 99.9
1, 2, 4, 5 - TTCB	0 $\pm$ 0	48 $\pm$ 2.4	108 $\pm$ 6.7	176 $\pm$ 14.0	294 $\pm$ 27.3	320 $\pm$ 28.2
10-day survival, %	90	78	40*	56*	0*	0*

Lee-Desu Analysis

10-day survival - test levels 2, 3, 4, and 5 (\*) significantly different from control ( $P < .01$ ).

Table 15. Survival and weight of week old flagfish exposed for 28 days to a triple chlorobenzene mixture (Interim Table).

Parameter	Test level					
	0(control)	1	2	3	4	5
chlorobenzenes, $\bar{X} \pm S. D. (\mu g/l)$						
1, 4 - DCB	0 $\pm$ 0	76 $\pm$ 7	179 $\pm$ 13	295 $\pm$ 38	547 $\pm$ 39	814 $\pm$ 83
1, 2, 4 - TCB	0 $\pm$ 0	80 $\pm$ 6	182 $\pm$ 13	299 $\pm$ 37	547 $\pm$ 38	751 $\pm$ 69
1, 2, 4, 5 - TTCB	0 $\pm$ 0	47 $\pm$ 3	104 $\pm$ 7	178 $\pm$ 19	313 $\pm$ 21	310 $\pm$ 50
28-day survival, %	88	80	84	44*	2*	0*
weight, mg ( $\bar{X} \pm S. D.$ )	65 $\pm$ 21	37 $\pm$ 13*	29 $\pm$ 11*	15 $\pm$ 5*	8(n=1)*	-

Lee-Desu Analysis

28-day survival - test levels 3, 4 and 5(\*) significantly different from control ( $P < .01$ ).

Anova/Duncan Analysis

growth - test levels 1, 2, 3, and 4 (\*) significantly different from control ( $P < .01$ ).

behaves like it did in the acute test, we have recently conducted a binary mixture test with 1, 4 - DCB and 1, 2, 4 - TCB to evaluate 10-day larval survival. We anticipate a detailed presentation of results and discussion on multiple chronic toxicity to be available in the final report on chlorinated benzenes, scheduled for release at the end of the current calendar year.

### 3. Bioconcentration.

Bioconcentration by fish of chlorinated benzenes should follow a trend of increasing bioconcentration potential with increasing chlorination. This generalized statement implies that the parameters used to quantify bioconcentration phenomena should be predictable on the basis of structure-activity relationships. Hence, the most-chlorinated compound studied, 1, 2, 4, 5 - TTCB, should yield the highest bioconcentration factor,  $K_B$ . The 1, 2, 4 - TCB isomer should yield the next highest  $K_B$  value, while 1, 4 - DCB should have the smallest  $K_B$ . Similarly, the uptake rate constant,  $K_1$  for these compounds should be in the following order of decreasing magnitude: 1, 2, 4, 5 - TTCB > 1, 2, 4 - TCB > 1, 4 - DCB. Conversely,  $K_2$  (clearance rate constant) should be in increasing order of magnitude: 1, 2, 4, 5 - TTCB < 1, 2, 4 - TCB < 1, 4 - DCB. From these initial parameter estimates, together with chemical information such as water solubility and octanol/water partition coefficients (Neely et al., 1974) we can adequately describe and predict the bioconcentration dynamics of the entire group of chlorinated benzene compounds.

An in-depth discussion of structure-activity relationships for the chlorobenzenes must be reserved for the final summary report on this project, scheduled for the end of the 1984 fiscal year. Although the actual bioconcentration testing with these compounds is complete, we are experiencing difficulties with the collection of chemical data. The problem of generating reliable water solubility data for hydrophobic organics has been previously addressed by our group (Todd et al., 1980). Calculated (theoretical) octanol/water partition coefficients are highly dependent on which author's mathematical formula that one uses. And experimentally-determined values are very sensitive to good technique, regardless of whether one uses a classical method (Neely et al., 1974) or a sophisticated method such as HPLC (Veith et al., 1979).

In keeping with the recommendations of the OECD Committee for the Chemical Testing Program, we have expressed our bioconcentration data on the basis of total body weight and lipid weight. The main advantage of the lipid format is that there appears to be a better correlation between residue and lipid weight than residue and total body weight (Konemann and van Leewen, 1980).

The lipid content for 4 to 5 month old juvenile flagfish, as determined in our laboratory, is  $8.5 \pm 0.34\%$  of total body weight. This figure allows us to calculate the conversion factor,  $100/8.5 = 11.8$ , which is used to determine bioconcentration parameters on the basis of lipid content. It is important to emphasize that lipid-based bioconcentration data were obtained by first converting the actual raw data

on individual whole fish samples prior to performing a Biofac analysis. Therefore, the lipid-based  $K_B$ ,  $K_1$  values and bioconcentration curves are not simply generated by multiplying whole flagfish, computer-derived numbers by the 11.8 conversion factor.

Whether or not a dose-additivity relationship can be determined from our results on single and multiple chlorobenzene bioconcentration in flagfish will require a considerable amount of additional data analysis. At the present point in time, we will simply present the available data.

The 1, 4 - DCB, of course exhibited the lowest bioconcentration potential of the three chlorobenzenes studied (Table 16, Fig. 5). The potential of 1, 2, 4 - TCB to bioconcentrate was about 10 times greater than 1, 4 - DCB on a whole fish basis (Table 17, Fig. 6). As expected, the tetrachlorobenzene isomer exhibited the largest  $K_B$  value, about 20 times greater than 1, 4 - DCB on a whole fish basis (Table 18, Fig. 7).

The same trend of increasing  $K_B$  value with increasing chlorination was readily observed in the triple chlorobenzene bioconcentration test.

$K_1$  values based on whole fish analysis were twice as large for 1, 2, 4 - TCB and 3 times larger for 1, 2, 4, 5 - TTCB, compared to  $K_1$  for 1, 4 - DCB. Conversely, clearance rate ( $K_2$ ) decreased by a factor of 2 through the series, DCB, TCB, TTCB (Table 19). Fig. 8 nicely demonstrates the relationships of these chlorobenzenes in terms of bioconcentration dynamics. The minimal scatter of data points indicates that the shapes of these curves are very precisely defined.

Lipid-based bioconcentration data from the triple chlorobenzene mixture test again confirms the consistent relationship of  $K_1$  and  $K_B$  values to increasing chlorination of the benzene ring (Table 20, Fig. 9).



Table 16. Biofac analyses of 1, 4 - dichlorobenzene bioconcentration in whole flagfish and flagfish lipid<sup>a</sup>.

PARAMETER	UNITS	$\bar{X} \pm S. D.$	
		Whole flagfish	Flagfish lipid
Water concentration during uptake	$\mu\text{g/l}$	$2.68 \pm 0.23^b$	
Uptake rate constant, $K_1$	$\text{days}^{-1}$	$291 \pm 26$	$4230 \pm 439$
Clearance rate constant, $K_2$	$\text{days}^{-1}$	$0.98 \pm 0.04$	$1.18 \pm 0.11$
Bioconcentration factor, $K_B$	-	$296 \pm 29$	$3590 \pm 498$
Time to 90% steady state	days	$2.34 \pm 0.10$	$1.96 \pm 0.18$
Time (1/2) for clearance	days	$0.70 \pm 0.03$	$0.59 \pm 0.05$
Heteroscedasticity parameter, $\gamma$	-	$0.82 \pm 0.23$	$0.48 \pm 0.16$

a)  $K_B, K_1 \text{ lipid} = 100/8.5 = 11.8$  ( $K_B, K_1$  body weight) and  $K_2 \text{ lipid} = K_2$  body weight.

b) equivalent concentration in  $\mu\text{mol/l} = 18.23 \pm 1.56 \times 10^{-3}$ .

Fig. 05. Bioconcentration of 1, 4 - dichlorobenzene in flagfish.

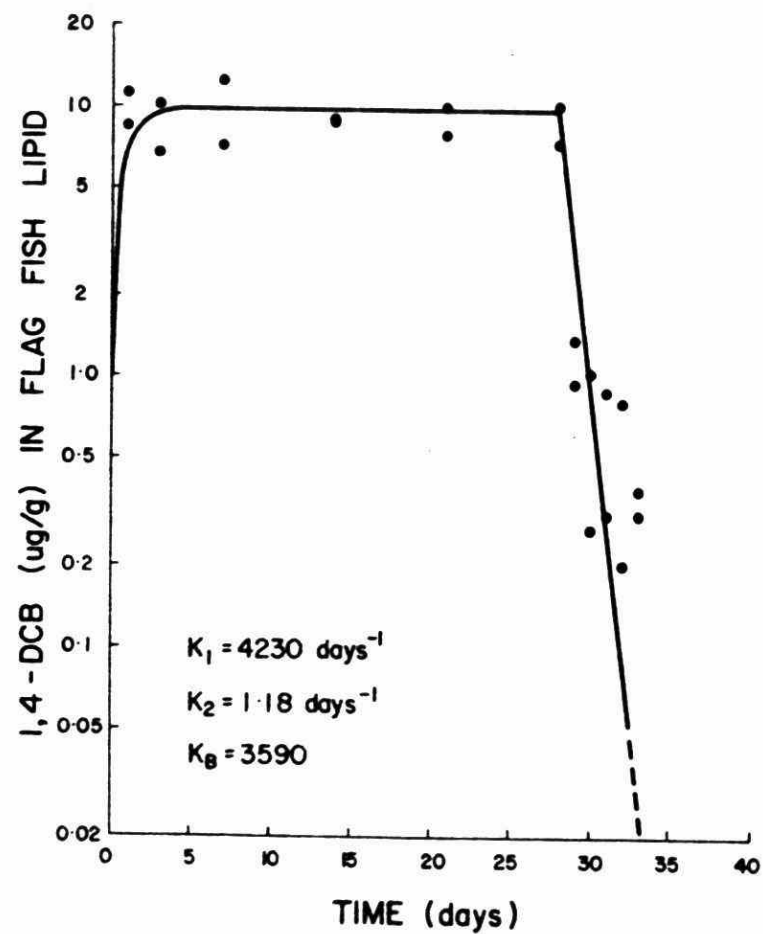
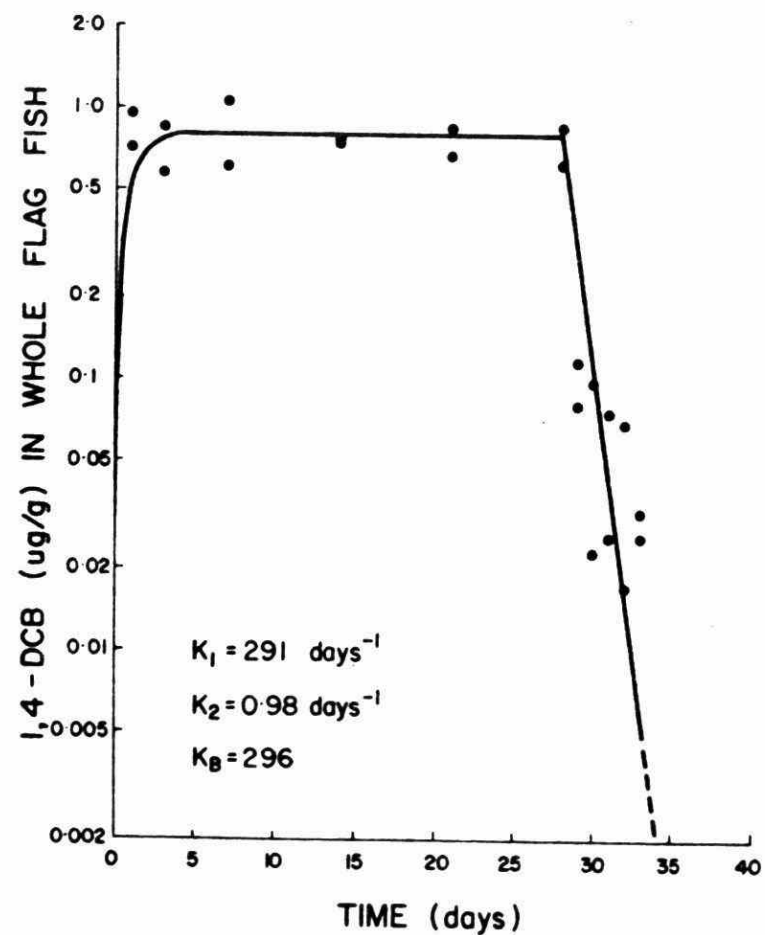


Table 17. Biofac analyses of 1, 2, 4 - trichlorobenzene bioconcentration in whole flagfish and flagfish lipid<sup>a</sup>.

PARAMETER	UNITS	$\bar{X} \pm S. D.$	
		Whole flagfish	Flagfish lipid
Water concentration during uptake	$\mu\text{g/l}$	$3.80 \pm 0.23^b$	
Uptake rate constant, $K_1$	$\text{days}^{-1}$	$1158 \pm 84$	$13660 \pm 987$
Clearance rate constant, $K_2$	$\text{days}^{-1}$	$0.57 \pm 0.01$	$0.57 \pm 0.02$
Bioconcentration factor, $K_B$	-	$2026 \pm 154$	$23911 \pm 1918$
Time to 90% steady state	days	$4.03 \pm 0.09$	$4.03 \pm 0.14$
Time (1/2) for clearance	days	$1.21 \pm 0.03$	$1.21 \pm 0.04$
Heterascedasticity parameter, $\gamma$	-	$1.98 \pm 0.10$	$1.98 \pm 0.43$

a)  $K_B, K_1 \text{ lipid} = 100/8.5 = 11.8 (K_B, K_1 \text{ body weight})$  and  $K_2 \text{ lipid} = K_2 \text{ body weight}$ .

b) equivalent concentration in  $\mu\text{mol/l} = 20.92 \pm 1.26 \times 10^{-3}$ .

Fig. 06. Bioconcentration of 1, 2, 4 - trichlorobenzene in flagfish.

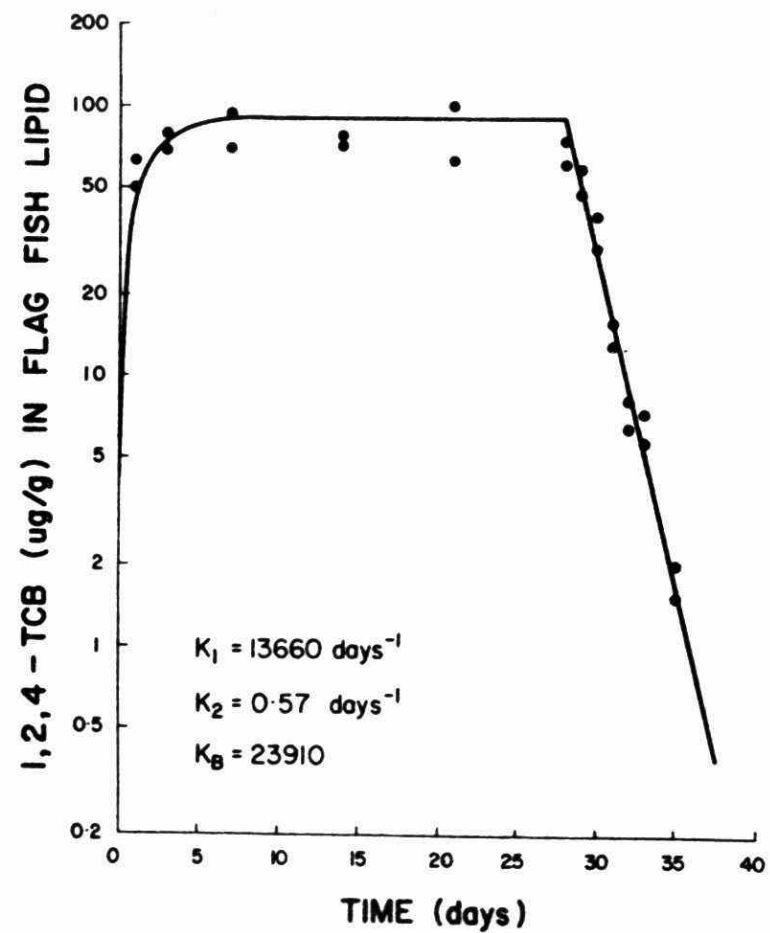
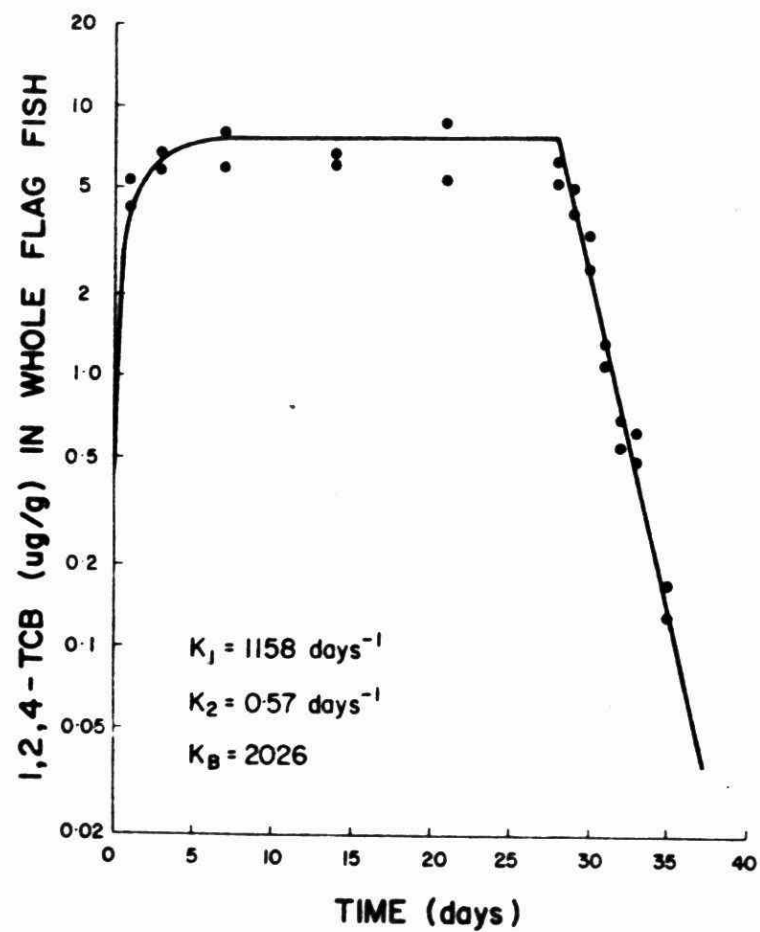


Table 18. Biofac analyses of 1, 2, 4, 5 - tetrachlorobenzene bioconcentration in whole flagfish and flagfish lipid<sup>a</sup>.

PARAMETER	UNITS	$\bar{X} \pm S. D.$	
		Whole flagfish	Flagfish lipid
Water concentration during uptake	$\mu\text{g/l}$	$3.02 \pm 0.29^b$	
Uptake rate constant, $K_1$	$\text{days}^{-1}$	$1630 \pm 246$	$17100 \pm 3185$
Clearance rate constant, $K_2$	$\text{days}^{-1}$	$0.40 \pm 0.03$	$0.34 \pm 0.04$
Bioconcentration factor, $K_B$	-	$4050 \pm 703$	$50300 \pm 11427$
Time to 90% steady state	days	$5.71 \pm 0.49$	$6.77 \pm 0.88$
Time (1/2) for clearance	days	$1.72 \pm 0.15$	$2.04 \pm 0.27$
Heteroscedasticity parameter, $\gamma$	-	$1.93 \pm 0.51$	$1.51 \pm 0.53$

a)  $K_B$ ,  $K_1$  lipid =  $100/8.5 = 11.8$  ( $K_B$ ,  $K_1$  body weight) and  $K_2$  lipid =  $K_2$  body weight.

b) equivalent concentration in  $\mu\text{mol/l} = 0.0140 \pm 0.0013 \times 10^{-3}$ .

Fig. 07. Bioconcentration of 1, 2, 4, 5 - tetrachlorobenzene in flagfish.

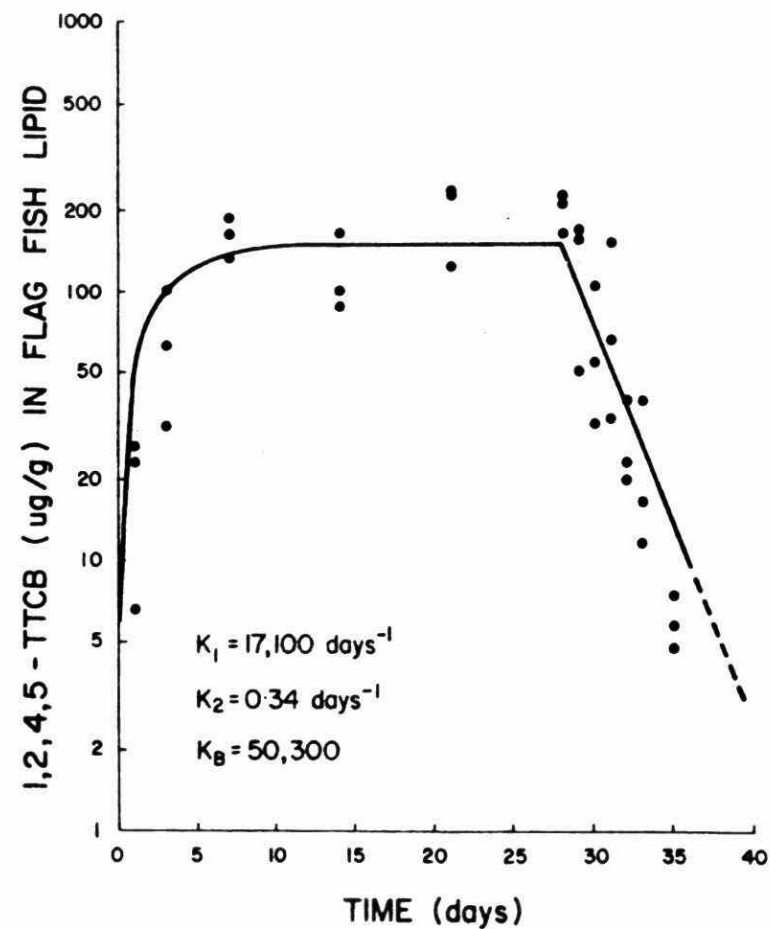
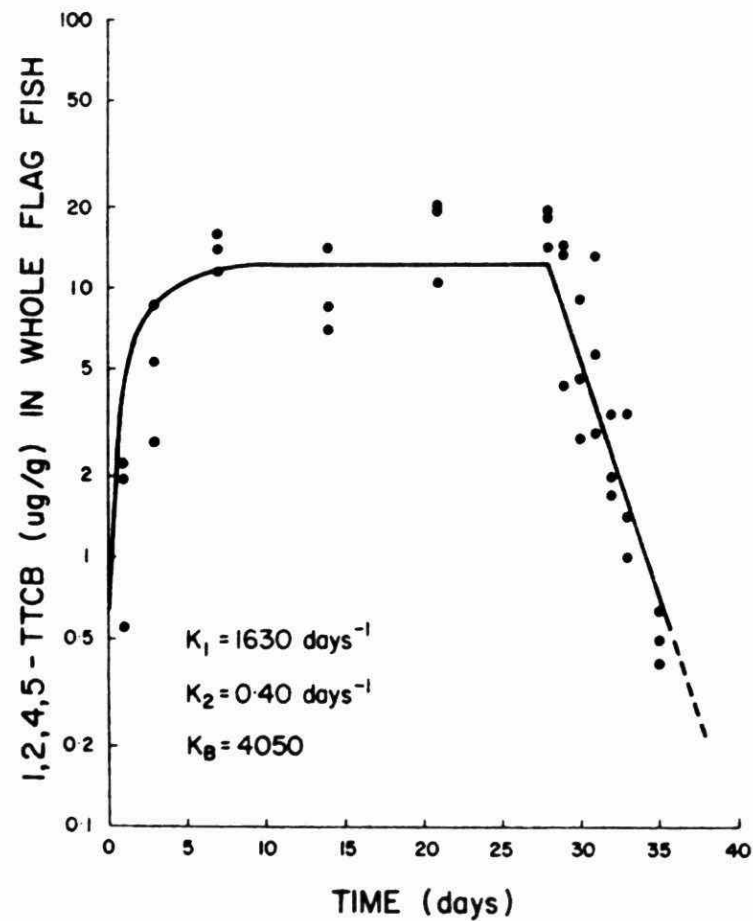


Table 19 Biofac analyses of 1, 4 - DCB, 1, 2, 4, - TCB and 1, 2, 4, 5 - TTCB  
triple mixture bioconcentration in whole flagfish.

PARAMETER	UNITS	$\bar{X} \pm S. D.$		
		1, 4 - DCB	1, 2, 4 - TCB	1, 2, 4, 5 - TTCB
Uptake water concentration	$\mu\text{g/l}$	$3.28 \pm 0.27$	$3.80 \pm 0.23$	$3.87 \pm 0.27$
Uptake rate constant, $K_1$	$\text{days}^{-1}$	$565 \pm 45$	$1158 \pm 84$	$1565 \pm 107$
Clearance rate constant, $K_2$	$\text{days}^{-1}$	$1.32 \pm 0.04$	$0.57 \pm 0.01$	$0.22 \pm 0.01$
Bioconcentration factor, $K_B$	-	$429 \pm 37$	$2026 \pm 154$	$7048 \pm 606$
Time to 90% steady state	days	$1.75 \pm 0.05$	$4.03 \pm 0.10$	$10.37 \pm 0.54$
Time (1/2) for clearance	days	$0.53 \pm 0.02$	$1.21 \pm 0.03$	$3.12 \pm 0.16$
Heteroscedasticity, $\gamma$	-	$2.10 \pm 0.38$	$1.98 \pm 0.10$	$1.24 \pm 0.45$

Fig. 08. Bioconcentration of 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB in whole flagfish exposed to a triple chlorobenzene mixture.

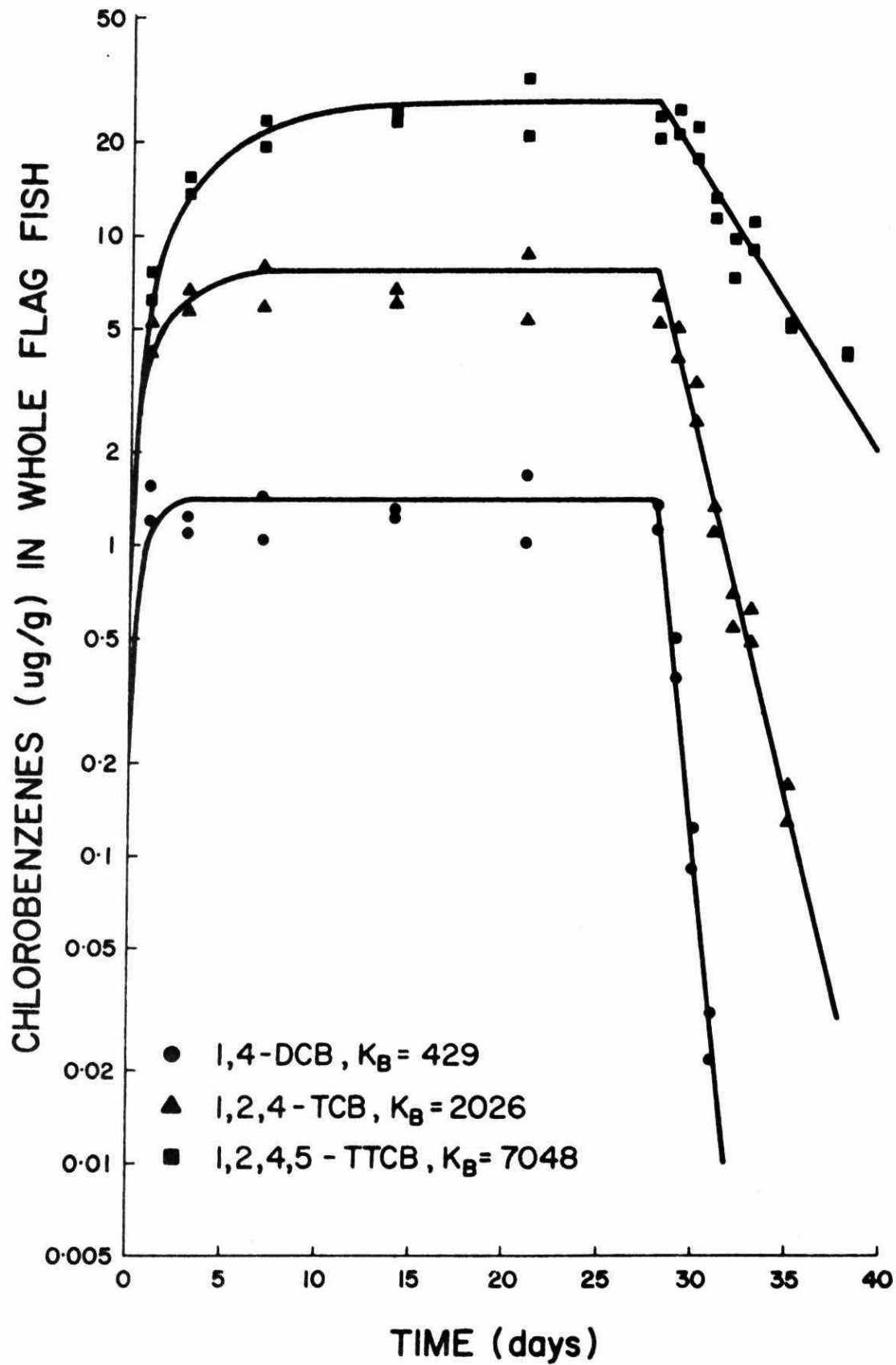




Table 20. Biofac analyses of 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB triple mixture bioconcentration in flagfish lipid<sup>a</sup>.

PARAMETER	UNITS	$\bar{X} \pm S. D.$		
		1, 4 - DCB	1, 2, 4 - TCB	1, 2, 4, 5 - TTCB
Uptake water concentration	µg/l	3.28±0.27	3.80±0.23	3.87±0.27
Flagfish lipid content	% weight	8.50±0.34	8.50±0.34	8.50±0.34
Uptake rate constant, $K_1$	days <sup>-1</sup>	6660±526	13,660±987	18,467±1263
Clearance rate constant, $K_2$	days <sup>-1</sup>	1.32±0.04	0.57±0.02	0.22±0.01
Bioconcentration factor, $K_B$	-	5066±428	23,910±1918	83,160±7147
Time to 90% steady state	days	1.75±0.05	4.03±0.14	10.37±0.54
Time (1/2) for clearance	days	0.53±0.02	1.21±0.04	3.12±0.16
Heteroscedasticity, $\gamma$	-	2.10±0.38	1.98±0.43	1.24±0.46

a)  $K_B$ ,  $K_1$  lipid = 11.8 ( $K_B$ ,  $K_1$  body weight) and  $K_2$  lipid =  $K_2$  body weight.

Fig. 09. Bioconcentration in flagfish lipid of 1, 4 - DCB, 1, 2, 4 - TCB and 1, 2, 4, 5 - TTCB from a triple chlorobenzene mixture.

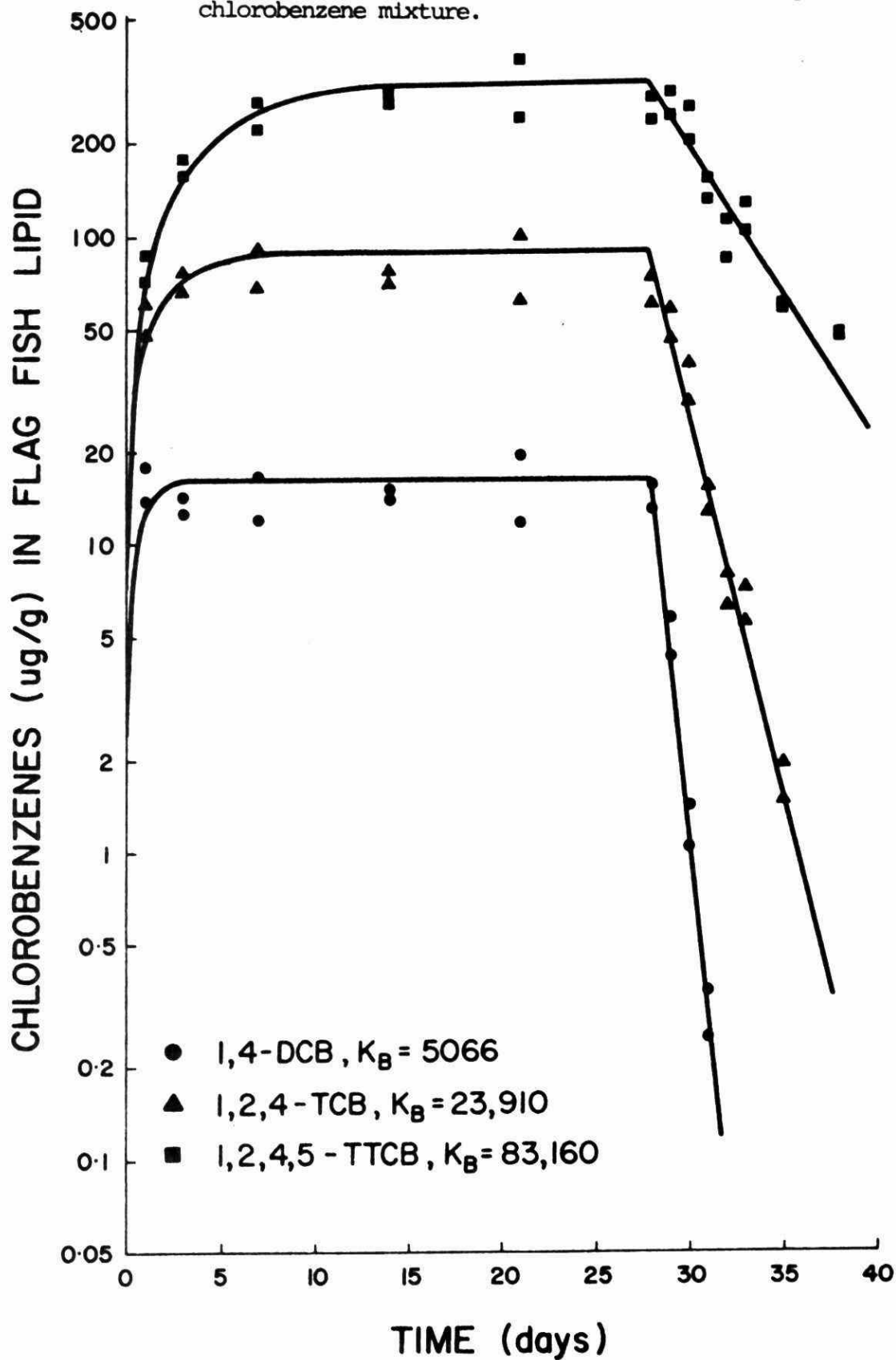


Fig. 10, a composite of the preceding two figures, has been included simply to demonstrate the tremendous difference in magnitude (y-axis scale) between bioconcentration in whole fish and in the primary target tissue, lipid.

### Conclusions

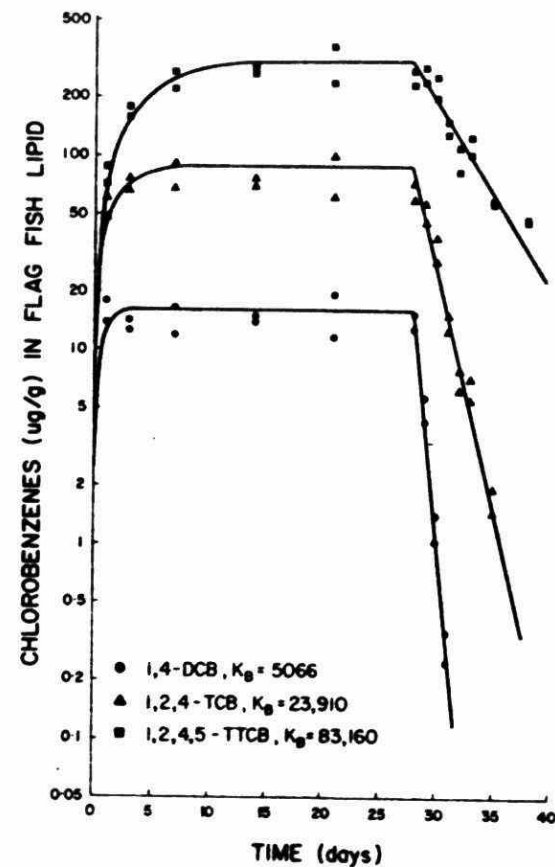
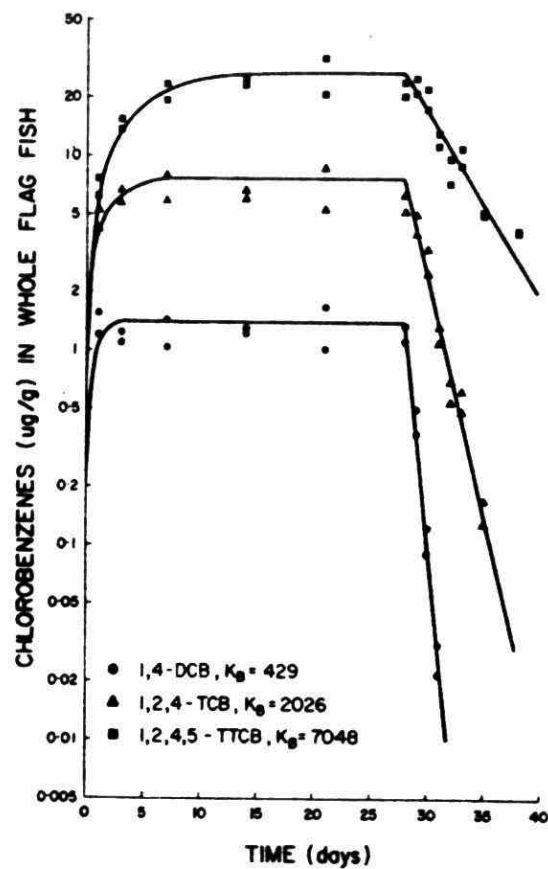
To make any conclusions regarding multiple toxicity and multiple bioconcentration of chlorinated benzenes in aquatic organisms would be premature at this stage of the study. We are reasonably confident, however, that further analysis of the experimental data collected in the mixture tests will either confirm or disprove the dose-additivity concept. The usefulness of this kind of experimental evidence to government regulatory agencies will undoubtedly prove to be invaluable as organic contamination of our freshwater systems becomes increasingly more complex.

### Acknowledgements

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Fig. 10. Bioconcentration of 1, 4 - dichlorobenzene, 1, 2, 4 - trichlorobenzene and 1, 2, 4, 5 - tetrachlorobenzene in flagfish exposed to a triple chlorobenzene mixture.



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THE AVAILABILITY OF PHOSPHORUS IN  
SEWAGE AND SEWAGE EFFLUENT TO  
A BLUE-GREEN ALGA, ANACYSTIS  
NIDULANS

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Abstract: Biologically available phosphorus, soluble reactive phosphorus, and total phosphorus of sewage and sewage effluent from several Ontario sewage treatment plants were measured. In a given sample soluble reactive phosphorus concentration often differed from biologically available phosphorus, but due to high variability from sample to sample average values were not significantly different. The efficiency of removal of biologically available phosphorus was highly variable, and no difference between tertiary treatment with alum or ferric chloride was detected. The proportion of the total phosphorus that was biologically available was also quite variable, and no significant differences were observed between alum and iron treated effluents.

Keywords: phosphorus, bioassay, sewage, effluents, bioavailability.

## INTRODUCTION

The performance of a sewage treatment plant with respect to phosphorus removal is currently based on the total phosphorus levels of its effluent. Although it is generally recognized that only a portion of the total is available for algal growth there is surprisingly little data that compares the chemically measured phosphate to biologically available phosphate (BAP) of sewage effluent. A standard algal assay procedure (AAP) has been available for some time (Maloney and Miller, 1975; American Public Health Association, 1975), but there are technical difficulties in performing bioassays on the particulate portion. In Sweden a variation of the AAP has been developed (Forsberg, 1972; Forsberg and Forsberg, 1972) and the biologically available phosphate has been assessed and compared to chemically measured phosphate. Data from several plants were summarized by Forsberg et al. (1978), and correlation coefficients between  $PO_4$ -P (presumably equivalent to soluble reactive phosphorus) and the algal growth potential ranged from +0.98 to -0.04. The lack of correlation in some plants was due to lower algal growth than expected from the chemical analysis. The authors attributed the effect to toxic substances in the effluent. Nonavailability of the chemically measured phosphate was apparently not considered.

It is well established that the soluble reactive phosphorus (SRP) of lake water is usually much greater than the biologically available phosphorus (BAP). Kuenzler and Ketchum (in Rigler, 1973) and Rigler (1966) used radioisotope techniques to show that in lab cultures and lake water the soluble reactive phosphate greatly overestimated the biologically available phosphate. Other evidence

from ion exchange studies (Rigler, 1973), differential filtration (Chamberlain and Shapiro, 1973) and extensive comparative analyses of lake water (Levine, 1975) have supported the view the SRP is not the same as BAP.

Studies of the phosphorus in urban and natural runoff, however, have found that BAP and SRP were very similar (Lee et al., 1980). The differences between investigators may have been due to the type of bioassays involved, but more likely it was simply a difference in the relative concentration of unavailable phosphorus that reacted in the chemical assay and the BAP concentration. The studies of the latter group involved relatively high concentration of BAP which may have 'swamped' the reactive but unavailable phosphate.

In sewage the levels of phosphate are high, but the substances that are believed to form reactive but unavailable phosphate complexes (iron, aluminum and calcium phosphates and metal organophosphate complexes; Chamberlain and Shapiro, 1973) may also be high. Therefore, it is possible that a significant portion of the chemically reactive phosphorus of sewage effluent is biologically unavailable. The purpose of this paper is to compare the bioavailability of phosphate to chemically assayed phosphate in the 'soluble' fraction of sewage and sewage effluent of several treatment plants and to make a preliminary assessment of the relative efficiency of various secondary and tertiary treatment methods in the removal of biologically available phosphate. Although ultimately both the 'soluble' and particulate fraction must be studied, only the 'soluble' fraction will be considered in this preliminary work. (These are technical impediments to bioassays on

the particulate fraction). Since 40 to 80% of the total phosphorus in sewage is in the soluble reactive form, it is an important source of phosphorus and is a suitable starting point for the study of the bioavailability of phosphorus in sewage.

## METHOD

### Sample collection

Samples from six sewage treatment plants in Ontario were collected at irregular intervals from May through September of 1980. Depending on the plant, samples of raw sewage, primary, secondary and final effluent were taken. Samples were returned to the Ministry of the Environment Laboratories (Rexdale) within 24 hours and processed immediately, or stored overnight at 4°C and processed the following day.

### Sample preparation

For a biological assay a sample must be free of organisms that might interfere, directly or indirectly with the activity of the test organism. Cowen and Lee (in Lee *et al.*, 1980) noted that in bioassays of samples which contained large amounts of organic carbon, large bacterial populations developed and depressed the growth of the test alga. They attributed the effect to competition for phosphorus. With the radiobiological assay the presence of bacteria could alter the isotope flux. This limitation obviously precludes bioassay of the particulate fraction, but since a major portion of the total phosphorus is soluble (see Results) useful information can be obtained from the liquid fraction. Particulates were removed by filtration through 0.2 µm polycarbonate filter (Bio-Rad) or a combination of glass fibre filter and the membrane

filter. Since, in most cases, the bioassays could not be performed immediately, the samples were sterilized by autoclaving at 121°C for 15 minutes. (Non-sterile samples usually developed bacterial populations within a few days which stripped the medium of phosphate). Samples were refrigerated at 4°C until assayed, usually within 1 to 2 weeks.

Total phosphorus and soluble reactive phosphorus analyses were done according to Stainton et al. (1974) using either a Technicon autoanalyzer by Ministry of Environment staff, or manually (autoclaved samples only) on a Bausch and Lomb spectrophotometer (Spectronic 88). The total phosphorus analyses were done on unfiltered samples, and 2 soluble reactive phosphorus analyses were done on each sample, one on the 0.2 µm filtered and autoclaved subsample and the other on a glass fibre filtered subsample. They will be designated SRPa and SRP respectively.

Bioassays were done as described by Mierle (1982). Samples were usually diluted 1/10 or 1/20, but sometimes no dilution was made if SRPa data indicated very low phosphate concentration.

## RESULTS

### Total phosphorus

The total phosphorus levels of the raw sewage were variable from sample to sample and plant to plant. The average values for plants ranged from 120 to 705 µM, and the average within-plant coefficient of variation was 39% (Table 1). The total phosphorus of the final effluent was equally variable, but the percent removed was relatively stable. For the 5 plants with secondary treatment facilities the average removal was  $86.1 \pm 1.2\%$  ( $\pm$  SEM). The average

coefficient of variation within secondary treatment plants was only 3.5% which suggests that most of the variation in the total phosphorus of the final effluent was due to variation in the input concentration of total P. There was no evident differences between the secondary plants in total phosphorus removal efficiencies.

#### Soluble reactive phosphorus

The soluble reactive phosphorus (glass fibre filtered, not autoclaved) data are presented in Table 2. The average concentrations of the raw sewage for the various plants ranged from 30 to 420  $\mu\text{M}$ . Within plants the sample to sample variability was somewhat higher than the total phosphorus levels, with an average coefficient of variation of 50%. The final effluent levels were 7 to 17  $\mu\text{M}$  for the secondary plants, with the same average coefficient of variation as the raw sewage. The proportion of soluble reactive phosphorus differed between some plants. In raw sewage the SRP/TP ratio ranged from 0.21 to 0.67. The ratio tended to increase in the final effluent, and ranged from 0.41 to 0.80. Within plants the SRP of the raw sewage may have been correlated to the total phosphorus level, for the average coefficient of variation of the ratio was only half the coefficient of variation of the concentration of SRP.

#### Effect of preparative technique on SRPa

The standard method of SRP analysis of sewage employs filtration through a glass fiber filter (usually Reeve Angel) which has a nominal pore size of about 1.2  $\mu\text{m}$ . For preparing samples for the bioassays filters with a smaller pore size (0.2  $\mu\text{m}$ ) were used to ensure complete removal of bacteria which might release phosphate during autoclaving. To determine if the difference in filters and the autoclaving had any effect the ratio of the two SRP measurements

was computed for each sample. A value of one would indicate no difference.

Generally the ratio was less than one (Table 3) which indicates that either the difference in filtration or the autoclaving removed some of the reactive phosphorus. Autoclaving might remove phosphate by precipitation, and occasionally precipitates were observed in autoclaved samples. Those samples, however, were not included in the analysis. Thus, it is likely that the difference was due to the smaller pore size. With one exception, the ratio was less in raw sewage samples than in final effluents which may indicate that raw sewage has a higher content of colloiddially bound phosphate that is molybdate reactive. The ratio of SRP's from the raw sewage of one plant (Plant 0) was consistently greater than one, which might be due to hydrolysis of organophosphates during autoclaving. These rather unexpected results in themselves suggest that the SRP of sewage is not simply a measure of dissolved orthophosphate.

BAP analysis: a test for interferences

As with any chemical analytical procedure a bioassay can be checked for interferences by making standard additions to samples. It would have been desirable to test all samples this way, but it was impractical to do so. A set of samples from one plant (P) were analyzed, however, with various additions. The sequence of values obtained for each sample were summarized by regressing the reciprocal of the rate constant against added phosphate concentration, and the slope from the sample was compared to the slope of the linear portion of the standard curve (see Mierle, 1982 for details). In three of the four samples the slope was depressed



about 14% and confidence limits indicate borderline significance (Table 4). Although the error in these samples was not large, the potential for greater error obviously exists and data interpretation should be made cautiously.

Removal efficiency of biologically available phosphate

A question of particular interest was whether any treatment method was better at removal of available phosphate than the others. The average effluent concentrations were substantially different from plant to plant, but the variation was also quite large, so that no significant differences in the concentration of BAP in the final effluent emerged between secondary plants. When expressed as an efficiency, i.e. the proportion of the BAP removed (as a percent), one plant (G) was significantly better than others. The difference was probably not related to the type of P removal (Fe), for another plant of the same type had a lower efficiency and was similar to plants using alum. The difference was probably related to the higher average concentration of BAP in the raw sewage of the plant. The low average efficiency of plant P was due to the low influent concentration, and to a few instances of negative efficiencies, i.e. effluents with concentrations greater than influent BAP concentration.

Since current effluent standards are based on total phosphorus concentration, another useful measure of BAP removal 'efficiency' is the BAP/TP ratio, the proportion of the total phosphorus in the effluent available for microbial growth. The mean ratios (Table 5) ranged from 0.25 to 0.63, but the variability was such that only the extremes (plants O and P) emerged significantly different at the 90% level. Both of these plants used alum, so



obviously the P removal method was not an important factor. Indeed it is possible that the difference is spurious, and that no real differences exist between plants.

#### Comparison of BAP to SRPa

One of the purposes of this study was to determine if soluble reactive phosphorus of sewage was a good measure of available phosphate, and if not, whether there were differences between treatment types. The ratio SRPa:BAP was used for comparison.

Values from sample to sample varied considerably, from less than one to greater than one. To be certain that analytical errors were not a significant component of the variation, five samples from various stages of one plant (G) were subjected to quadruplicate analysis of BAP and SRPa. Mean values and confidence limits are presented in Table 6. In two samples, B and D, the ratios were clearly greater than one, and a third, E, which was also greater than one had very large confidence limits due to one very large ratio. (Wide confidence limits at low concentrations were not unexpected, for the relative error is large at low available phosphate - see Mierle, 1982). Exclusion of the one deviant value yielded a mean ratio of  $2.64 \pm 2.34$  ( $\pm 90\%$  C.L.). It is likely that the ratio of sample E was also greater than one.

With regard to individual plants, the mean ratios were not significantly different from each other, nor significantly different than one (Table 7). This does not mean that real differences in BAP and SRP did not exist. Most of the raw sewage samples had high enough phosphorus concentrations that analytical error was unimportant, and individual sample ratios (as high as 7.9) reflect real differences and the wide confidence limits reflect real variation in the

samples. The same may be true of the sewage effluents (c.f. replicate analyses in Table 6), although because of the generally low phosphorus concentration in these samples, analytical error would have contributed significantly to the variability. When all the individual sample ratios are summarized in a grand mean, the mean is significantly different from one in both raw sewage and effluents, i.e. on average SRP overestimates BAP. There was a tendency for the SRP:BAP ratio to decrease from raw sewage to final effluent, but the decline was not statistically significant for individual plants nor for all samples combined.

The SRPa and BAP data are summarized in a scatter diagram, (Fig. 1) which included data from intermediate treatment stages as well as data from raw sewage and final effluents. Although there is considerable spread in the data points, there is an obvious tendency for points to lie below the line of equivalence. That is, SRP tends to overestimate the biologically available phosphate of sewage samples.

## DISCUSSION

Several investigations on the availability of phosphate in natural waters (Rigler, 1966, 1968; Levine, 1975) have found that SRP grossly overestimated the biologically available phosphate. The results of this paper show that SRP tends to overestimate available phosphate in sewage and sewage effluent as well, although the difference is not the 10-100 fold difference reported by Rigler (1966) or Levine (1975) for lakes, and that sometimes BAP was greater than SRP. Other investigators (Walton and Lee, 1972; Cowan and Lee, in Lee et al., 1980) have found fairly good agreement between SRP and BAP of natural waters, but their studies differed in two important respects from the others. First, the concentration of SRP was much higher in their water samples. Lee et al. (1980) suggested that the difference in results may have been due to the relative amounts of orthophosphate and reactive but unavailable phosphate. If the interfering substances were relatively constant the error would be negligible at high orthophosphate concentration. A second important difference was the type of assay used. Rigler and Levine used a kinetic radiobiological assay of short duration, and therefore they measured only the rapidly available phosphorus. Lee, Cowen and Walton used the batch algal assay procedure, which uses the yield of algae after about two weeks of growth to measure the available phosphate. With the latter method the algae obviously have a much greater time to extract phosphate from complexes that are not readily available. There is little data on which to judge whether one or the other or both are important, but the findings of Chamberlain and Shapiro (1969) are relevant.

They used a bioassay based on the removal of phosphate from water samples over a 1-2 hour period. They found good agreement between SRP and BAP, but as with Lee's studies many of their samples had relatively high concentrations of phosphate. Since both the extraction technique and growth bioassays gave similar results under similar conditions even though the duration of the experiments were widely different it seems likely that the difference in results of the various investigators was not due to the rate at which the algae extract phosphate from complexes, but to the ratio of 'free' orthophosphate to complexes or compounds of phosphate. At moderately high levels (eg.  $> .16 \mu\text{M}$  or  $> 5 \text{ ppb P}$ ) SRP is probably a reasonable measure of orthophosphate in lake waters.

Although the available phosphorus concentration in sewage and sewage effluents is high compared to lakes, the results of this study suggest that unavailable but reactive complexes are also high. This observation is not incompatible with the postulated nature of these substances. Rigler and Chamberlain (Chamberlain and Shapiro, 1973) have found that a large fraction of the SRP from lake water could be removed by refiltration through 0.01 to  $0.1 \mu\text{m}$  filters, an indication that much of the interfering phosphate was in colloidal-like particles. Chamberlain and Shapiro suggested three possible compositions for these particles: calcium phosphate, ferric phosphate and organo-metallic phosphate complexes. The latter is particularly well supported by the work of Lean (1973) on lake water. In sewage ferric and aluminum phosphate are formed as part of the phosphate removal process, and it seems quite possible that some is not precipitated but is held in suspension as organo-metallic phosphate complexes. The high concentration of

organic matter in sewage would obviously favour the latter. However, large differences were observed in raw sewage (before iron and aluminum additions), so other types of complexes (e.g. calcium phosphate must also be important. Elucidation of the nature of the complexes might help predict those situations where reactive but unavailable phosphorus complexes form.

The effect of filtration technique and the data on the phosphorus availability are consistent with the above considerations. Sewage samples that had been filtered through 0.2  $\mu\text{m}$  pore filters had less SRP than samples filtered through glass fibre filters. This observation suggests that some of the SRP in the glass fibre filtrate was due to small particulate complexes. Since the complexes would probably be of a heterogeneous size range, some very small complexes were probably present in the 0.2  $\mu\text{m}$  filtrate as well. The BAP of the 0.2  $\mu\text{m}$  filtrate was usually lower than the SRP, and the difference may have been due to such complexes.

In some samples the available phosphorus was greater than the SRP. This can be explained by the presence of organophosphates or polyphosphates. Although organophosphates have often been considered a source of molybdate reactive phosphate, evidence reviewed by Chamberlain and Shapiro (1973) suggests that phosphoesters are only slowly hydrolyzed under conditions of the assay. In a bioassay, however, phosphoesters and polyphosphates would probably be quickly hydrolyzed by the phosphatases produced by algae when phosphate starved (Kuenzler, 1965; Clesceri and Lee, 1965). The released phosphate could then be quickly utilized. In sewage one might expect that few organophosphates and polyphosphates would remain because the microorganisms of the activated sludge

would have ample time to hydrolyse any phosphoesters present. However, phosphatases are inducible enzymes in algae (Kuenzler, 1965) and probably the same is true of bacteria. Since phosphate is not limiting in sewage, phosphatase synthesis would be repressed, and organophosphates and polyphosphates might persist. The samples with greater BAP than SRP suggests that they were indeed present. Their importance may not be fully evident, however, for the SRP:BAP ratio is influenced by both reactive unavailable phosphate complexes and available unreactive organophosphates. The former could mask the latter (and vice versa) in the ratio, and as indicated above reactive unavailable complexes may be important constituents of sewage.

Currently the effluent standard for phosphorus is based on total phosphorus. This measure has the virtue of being well defined and allows 'worst case' predictions of the effect of a given level of phosphorus release. However, from the standpoint of determining the optimum cost:benefit ratio it would be better to use biologically available phosphorus. The potential danger in that approach is the difficulty of assessing the adequacy of the BAP analytical technique. Ultimately no lab procedure can exactly mimic all the processes that occur in nature, especially with regard to the fate of the particulate fraction of the effluent. Probably most of the particulate phosphate never becomes available to other organisms, but since there is no data on this subject that hypothesis is quite speculative. The soluble fraction is more amenable to analysis, but even with it one must accept potential inadequacies of the test organism as a representative of natural populations. Nonetheless, the large difference that were sometimes observed between biologically available phosphorus and total phosphorus observed in this study suggests that the topic merits further research before unnecessary investments are made in improving total phosphorus removal.

#### SUMMARY

This study demonstrated that soluble reactive phosphorus and biologically available phosphorus can be markedly different in sewage. On average, however, the difference is relatively small (especially in effluents) compared to lake water. It was hoped that some patterns in bioavailability might emerge with respect to treatment type, particularly with regard to aluminum verses iron for phosphorus removal, but the great variability from sample to sample (ie. temporal variability) overshadowed any plant-to-plant differences that might have existed. This observation suggests that even if one method is better than another at one point, differences are averaged out over time. However, a more detailed study, preferably in a plant with parallel operation is obviously necessary to resolve the issue.

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Table 1	Total phosphorus levels of the study plants. There was considerable temporal variability in total phosphorus of the raw sewage and final effluent, but the removal efficiency was relatively constant. C.V. = coefficient of variation, %.
Table 2	Soluble reactive phosphorus concentrations of glass fibre filtrates. Roughly half of the total phosphorus passed through the filter and reacted with molybdate, but considerable temporal and plant to plant variation was observed. C.V. = coefficient of variation, %; C.L. = 90% confidence limits. STP key and sample sizes as in Table 1.
Table 3	Comparison of soluble reactive phosphorus concentrations of autoclaved 0.2 $\mu$ m polycarbonate filter filtrates to reactive phosphorus of glass fibre filters. The data suggests that a portion of the reactive phosphorus can be removed by small pore size filters. SPT key and sample sizes as in Table 1.
Table 4	A test for interfering substances in samples from one STP. To each sample a series of six standard additions were made (0 to 300 nM P) from which a curve analogous to the standard curve was constructed. The presence of an interferent (a substance that increases or decreases the rate of P uptake by the algae) is indicated by a difference in the slope of the standard curve and the slope of the curve derived from standard additions to the samples.
Table 5	Biologically available phosphorus of the raw sewage and final effluents. There was no obvious differences removal efficiencies between alum and iron, and no convincing differences existed between plants. STP key and sample sizes as in Table 1.
Table 6	Test of the replicability of the assays. The mean and 90% confidence limits of 4 replicate analyses show the analytical error is significant only at low phosphate levels, but even in that case significant differences between BAP and SRP exist.
Table 7	Comparison of soluble reactive phosphorus of autoclaved, 0.2 $\mu$ m polycarbonate filtrates to the biologically available phosphorus. Although for individual plants the ratio was not significantly different from one, overall there was a significant tendency for SRP to overestimate BAP, especially in raw sewage. STP key and sample sizes as in Table 1.

Table 1

STP	Type	P removal	n	Total Phosphorus		Final Effluent μM C.V.	Removal %	Efficiency C.V.	
				Raw Sewage μM	C.V.				
G	E.A.	Fe	6	145	24	19	51	87.2	4.37
N	C.S.	Fe	4	120	38	21	30	81.8	5.50
O	Cv	Alum	5	148	60	19	29	88.2	1.10
P	C.S.	Alum	5	163	29	20	38	88.0	4.63
M	P	Fe	7	705	42	174	60	74.3	22.1
B	H.R.	Alum	6	319	42	35	42	85.2	2.02
Mean:					39%		38%	86.0	3.52

Keys:

STP  
 G - Gravenhurst  
 N - Port McNicol  
 O - Orangeville  
 P - Penetanguishe  
 M - Midland  
 B - Bradford

Type  
 E.A. = Extended aeration  
 C.S. = Contact stabilization  
 Cv. = Conventional  
 P = Primary  
 H.R. = High rate

Table 2

STP	Soluble reactive phosphate					SRP/TP					
	Raw Sewage μM	C.V.	Final Effluent μM	C.V.	Ratio	Raw Sewage C.L.	C.V.	Ratio	Final Effluent C.L.	C.V.	
G	97	32	7.3	66	0.67 ±	0.13	19	0.41 ±	0.15	34	
N	75	44	17	30	0.63	0.14	17	0.66	0.38	42	
O	86	44	16	47	0.48	0.20	22	0.77	0.47	31	
P	30	63	10	56	0.21	0.07	25	0.49	0.22	36	
M	421	66	146	82	0.61	0.21	37	0.80	0.15	20	
B	68	50	13	49	0.21	0.07	32	0.54	0.16	48	
Mean:		50		50			25			38	

Table 3

STP	SRPa/SRP			
	Raw Sewage		Final Effluent	
	Ratio	90% C.L.	Ratio	90% C.L.
G	0.738	± 0.141	0.940	± 0.383
N	0.602	0.0758	0.834	0.206
O	1.22	0.238	0.720	0.221
P	0.501	0.191	0.751	0.362
B	0.830	0.222	0.988	0.0913
M	0.260	0.108	0.500	0.218

Table 4

	Slope	90% C.L.	95% C.L.
Standards	21.3	$\pm 1.35$	$\pm 1.94$
Raw sewage	18.1	0.92	1.20
Digester	18.4	2.02	2.63
Contact chamber	18.5	0.79	1.03
Final effluent	20.0	3.13	4.6

Table 5

TP	Raw Sewage BAP 90% C.L. μM	Final Effluent BAP 90% C.L. μM	Removal Efficiency BAP 90% C.L. μM	BAP/TP Final Effluent Ratio 90% C.L.
G	66 ±11.7	4.8 ±1.8	91.2 ±1.8	0.32 ±0.19
N	23 7.2	7.4 4.3	65.6 11.8	0.43 0.40
O	39 17.7	13.0 4.1	67.1 5.0	0.63 0.21
P	14 8.8	5.2 4.2	18.4 42.6	0.25 0.16
B	- -	18.0 14.1	- -	0.41 0.19
M	46 24.1	28.2 12.7	44.9 7.5	0.33 0.16

Table 6

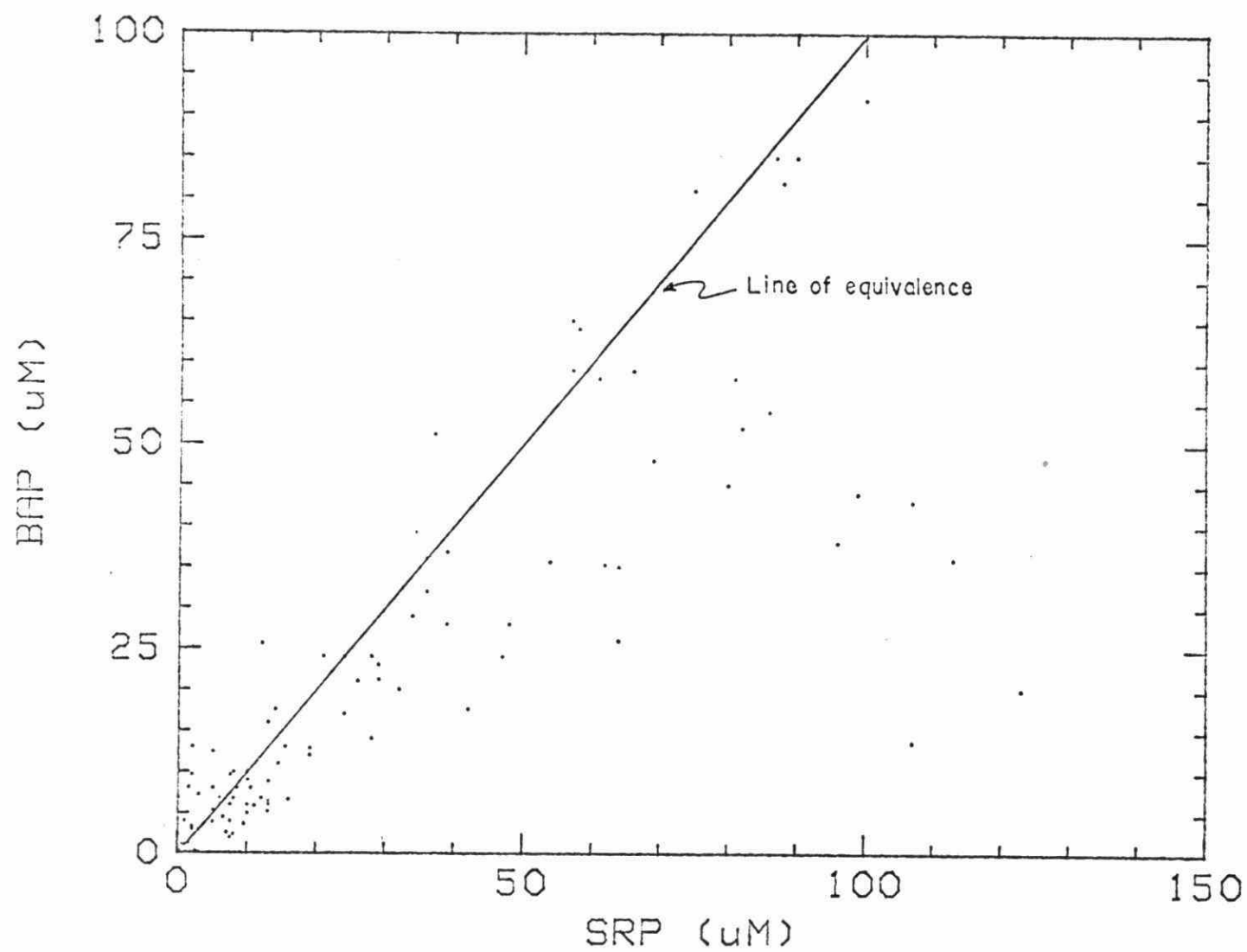
	Sample									
	A		B		C		D		E	
Mean SRP	57.3	±0.2	7.3	±0.3	60.8	±1.4	15.7	±0.5	10	±0.0
Mean BAP	59.4	4.8	1.7	0.8	58.4	2.5	8.3	2.5	3.7	3.8
Mean SRP/BAP	0.969	0.079	4.91	2.5	1.04	0.07	1.99	0.54	7.7	11.9
Mean SRP/Mean	0.996		4.29		1.04		1.90		2.71	



Table 7

STP	SRPa/BAP Raw Sewage		Final Effluent	
	Ratio	90% C.L.	Ratio	90% C.L.
G	1.13	±0.37	1.10	±0.53
N	1.43	0.64	1.09	0.28
O	4.07	3.11	0.97	0.54
P	1.23	0.65	1.74	0.94
B	-	-	0.98	0.28
M	2.40	2.07	1.74	1.18
Grand Mean	1.94	±0.58	1.30	±0.24

Fig. 1. Scatter diagram of BAP and SRP of all sewage samples analyzed. Although there is considerable spread in the data, there is a noticeable tendency for the points to lie below the line of equivalence.



DISSOLVED OXYGEN DEPLETION IN HAMILTON HARBOUR:

MODEL DEVELOPMENT & PREDICTIONS

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## ABSTRACT

The bottom waters of Hamilton Harbour are close to anoxia for most of the summer as a result of bacterial oxidation in the water column of reduced carbon, nitrogen and sulfur compounds from industrial and municipal sources or produced in situ, as well as oxygen demand exerted by the sediments. These oxygen depletion processes have been combined with the major sources (reaeration, photosynthesis and mass exchange with Lake Ontario) in a two-layer horizontally well-mixed dissolved oxygen model. The model has been calibrated to existing harbour conditions between 1976 and 1980, and sensitivity tests performed on the values of several important rate coefficients. The main limitation in the model is that all reduced nitrogen demand is considered to be due to ammonia loadings from industrial and municipal sources and internal loadings are neglected.

## INTRODUCTION

Hamilton Harbour (Figure 1) is a semi-enclosed body of water located at the extreme west end of Lake Ontario. It is roughly triangular in shape, with a surface area of  $2.1 \times 10^7 \text{ m}^2$  and a volume of approximately  $2.8 \times 10^8 \text{ m}^3$ . The harbour is separated from Lake Ontario by a sandbar through which passes the Burlington Ship Canal, which is approximately 107m wide and 9.5 m deep. As a result of extensive wastewater input from industries and municipal sewage treatment plants, the harbour is highly eutrophic and develops a severe dissolved oxygen depletion problem every summer, with the bottom waters approaching anoxic conditions.

The harbour has been extensively studied by the Ontario Ministry of the Environment since 1972 <sup>(1)</sup>. Regular weekly profiling (April to November) at the 4 major water quality stations (Figure 1) was performed from 1975 to 1980 <sup>(2,3,4)</sup>. Figures 2(a) and (b) show epilimnetic and hypolimnetic dissolved oxygen (D.O.) concentrations at stations 4, 258 and 270 and their average during 1976. Station 252 was not included due to its shallow depth. Important observations in these figures include: (a) considerable variability between stations, caused at least partly by horizontal variations in thermocline depth, and hence depth of D.O. concentration decline. (b) The rapid decline in both epilimnetic and hypolimnetic D.O. in May and June. From June to September, hypolimnetic values are consistently below the Provincial Water Quality Objectives ( $5 \text{ mgL}^{-1}$  for warm-water biota and  $6 \text{ mgL}^{-1}$  for cold-water biota at  $10\text{-}15^\circ\text{C}$ , which is the observed range of summer hypolimnetic temperatures). Anoxic or near-anoxic conditions exist in the lower hypolimnion for much of this period. (c) Epilimnetic D.O. values are almost always below saturation, particularly in early to mid-summer. (d) Incursions of oxygenated hypolimnetic water from Lake Ontario during the summer produce short-term increases in hypolimnetic D.O., most pronounced at the east end of the harbour (station 4). (e) Below-saturation conditions persist until late autumn. Measurements in 1980 indicated that even as late as mid-December, average harbour D.O. is only 85-90% of saturation.

Results for other years show similar characteristics. No significant year-to-year trend exists. Consequently, all data collected from 1975 to 1980 were averaged at 10-day intervals and are plotted for epilimnion (0-6m) and hypolimnion (10m-bottom) in Figure 3. Error limits are defined as plus or minus two standard errors.

In 1976, Polak and Haffner <sup>(8)</sup> measured rates of oxygen depletion at the sediments and in the water column in Hamilton Harbour. They obtained equations for the dependence of oxygen depletion rate on D.O. concentration, and constructed an oxygen budget. They estimated that about 80% of the oxygen depletion occurred in the water column, and the remainder in the sediments.

The oxygen in the water is consumed by biological processes that take place both in the water column and at the sediment surface. The main oxygen demand is due to bacterial oxidation of reduced carbon, nitrogen and sulfur compounds, which are present in the effluent from industry and the municipalities, or produced in situ by phytoplankton growth. Oxygen is added to the epilimnion from photosynthesis and atmospheric reaeration, and from the inflow of oxygenated water through the canal and from tributaries. In July and August, flow from the lake prevents continuous anoxia in the hypolimnion (Fig. 2a and 2b). Since the water column is unstable, vertical mixing is pronounced and oxygenated water is mixed into the hypolimnion and oxygen-depleted water is mixed into the epilimnion.

Lake-harbour interactions and their effect on harbour dynamics are discussed more fully elsewhere <sup>(5,6,7)</sup>.

#### LABORATORY MEASUREMENTS OF WATER COLUMN OXYGEN DEMAND

From June 1979 to October 1980, a series of laboratory measurements were conducted by Dr. M. A. Zarull (Water Resources Branch, MOE) to measure the water column oxygen demand (WCOD) and partition it among reduced carbon, nitrogen and sulfur.

Water samples were collected biweekly from 12m depth at station 258 and filtered through 10  $\mu$  Nitex mesh to remove algae and some particulate matter. The water was transported to the lab in an air-tight cooler and the experiments set up within two hours of collection.

Water samples were placed in blackened flasks with necks tapered to accept the tips of YSI oxygen probes. The flasks were placed in a constant temperature bath held at the ambient harbour temperature. The water in the flasks was stirred by teflon-coated stirring bars inside the flasks. Oxygen concentrations were recorded for 2 to 12 days, or until the oxygen content reached 1  $\text{mgL}^{-1}$ .

Three flasks were run during each experimental period. One flask (A) contained no additives, another (B) contained 3 mg 1-allyl-2-thiourea as a nitrification inhibitor, and the third (C) was adjusted to pH 4 with 0.1 N HCl. This should give sulfur demand only. Assuming that there are no other significant oxygen-demanding chemical or microbial processes, then

$$\text{reduced carbon demand (CBOD)} = B - C$$

$$\text{nitrification (NBOD)} = A - B$$

$$\text{reduced sulfur demand (SBOD)} = C$$

The results of biweekly tests showed that the oxygen demand rates increased and decreased dramatically from one sample period to the next. This was especially true in 1979, when nitrification frequently represented only very small portions of the total demand. Because the variation was smaller, and because more complete temporal coverage was obtained in 1980, only the 1980 results are presented (Table 1). To smooth out the fluctuations, the results were averaged over 2-month periods and converted to equivalent 20°C values using equation (8) (see model section) and  $\theta$  values of Freedman et al (9).



Except during the fall (Sept.-Oct.) period, the CBOD decay constant  $R_2$  was fairly constant at about  $0.09 \text{ day}^{-1}$ . The NBOD decay constant increases gradually as the season progresses, apparently reflecting the growth of the harbour nitrifier population. If temperature were the sole variable governing the value of  $R_3$  between January and August, an improbably high  $\theta$  value of 1.35 would be needed. The sulfur decay rate was apparently highest in the spring and fall; the reason for this rather unexpected seasonal variation was unknown.

#### DISSOLVED OXYGEN MODEL

A model was developed to describe the oxygen regime in the harbour and to predict changes in the regime if inputs from industry and municipalities are changed. The model considers the major sinks of oxygen to the harbour, reduced carbon (CBOD), nitrogen (NBOD) and sulfur (SBOD) compounds in the water column, plus sediment oxygen demand (SOD). Separate mass balance models for CBOD and NBOD are interlinked to the oxygen model. The reduced nitrogen demand is considered to be due to ammonia loadings from industrial and municipal sources and the reduced carbon demand due to CBOD loadings and to internal production of CBOD from photosynthesis. Since reduced sulfur loadings are not available, demand rates based on laboratory measurements of oxygen depletion due to reduced sulfur are used. The harbour is assumed to be horizontally well-mixed at all times. During spring and fall it is also vertically well mixed and is thus treated like a continuously-stirred tank reactor (CSTR) with vertical sides and a depth of 13 m (mean harbour depth). During the summer (thermal stratification), the epilimnion and hypolimnion are treated as separate CSTRs with the thermocline at 7 m depth. Convective transport, induced by exchange with Lake Ontario, moves deoxygenated hypolimnion water to the epilimnion. Diffusion between the layers, as well as settling of particulate oxygen-demanding material from the epilimnion to hypolimnion, and from the hypolimnion to the sediments, were also included.

The basic equation for dissolved oxygen for each layer is identical, except that photosynthesis and reaeration are applied only to the surface layer and sediment oxygen demand only to the bottom layer. The basic equation for either layer is as follows:

$$\frac{dC}{dt} = R_1(C_s - C) - R_2B - R_3N - R_4 + R_5 \left(\frac{A}{V}\right) + \frac{(\text{load})}{V} - \frac{E}{d^2}(C - C^*) - \frac{A}{V}(\text{SOD}) \quad \dots (1)$$

- where
- $C$  = dissolved oxygen concentration ( $\text{mg L}^{-1}$ )
  - $C_s$  = saturated dissolved oxygen concentration ( $\text{mg L}^{-1}$ )
  - $C^*$  = dissolved oxygen concentration in other layer
  - $B$  = CBOD concentration ( $\text{mg L}^{-1}$ )
  - $N$  = NBOD concentration ( $\text{NH}_3 \times$  a stoichiometric factor)( $\text{mg L}^{-1}$ )
  - $R_1$  = rate constant for reaeration ( $\text{day}^{-1}$ )
  - $R_2$  = rate constant for CBOD decay ( $\text{day}^{-1}$ )
  - $R_3$  = rate constant for NBOD decay ( $\text{day}^{-1}$ )
  - $R_4$  = rate of oxygen consumption by reduced sulfur compounds ( $\text{mg O}_2 \text{ L}^{-1} \text{ day}^{-1}$ )
  - $R_5$  = rate of oxygen production due to net photosynthesis ( $\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ )
  - $\text{SOD}$  = rate of oxygen consumption due to sediment oxygen demand ( $\text{g m}^{-2} \text{ day}^{-1}$ )
  - $A$  = harbour area ( $\text{m}^2$ )
  - $V$  = harbour volume (epilimnion or hypolimnion during stratification)( $\text{m}^3$ )
  - $E$  = diffusion coefficient,  $\text{m}^2 \text{ day}^{-1}$
  - $d$  = thickness of top layer, m
  - (load) = net input of dissolved oxygen to the harbour from external sources and sinks, including exchange with Lake Ontario, and vertical exchange and diffusion during the stratified period ( $\text{g day}^{-1}$ ). In the CBOD and NBOD equations, the respective loadings are substituted.

This equation can be integrated over a finite time step length  $\Delta t = t_2 - t_1$ , if it can be assumed that B, C, and N in the reaeration and DO-dependent SOD terms are constant over this time interval.

Upon integration and rearranging, we obtain:

$$C_2 = C_1 + R_1 \Delta t (C_s - C_{1\frac{1}{2}}) - \Delta t (R_2 B_{1\frac{1}{2}} + R_3 N_{1\frac{1}{2}} + R_4) + \frac{A}{V} \Delta t (R_5 - SOD) + \frac{(load)}{V} \Delta t - \frac{E \Delta t}{d^2} (C_{1\frac{1}{2}} - C_{1\frac{1}{2}}^*) \quad \dots(2)$$

where subscript 1 = quantity at time  $t_1$   
 2 = quantity at time  $t_2$   
 1 1/2 = approximated average concentration over time interval between  $t_1$  and  $t_2$

As already stated, (load) is the net loading to the harbour and is evaluated as

$$(load) = \sum C_{in} Q_{in} - \sum C_{out} Q_{out} \quad \dots(3)$$

These summations are carried out over all inflows and outflows to the harbour;  $C_{in}$  and  $C_{out}$  are inflow and outflow DO concentrations ( $mg\ L^{-1}$ ) and  $Q_{in}$  and  $Q_{out}$  are inflow and outflow water volumes ( $m^3\ day^{-1}$ ). The outflow concentration  $C_{out}$  is set equal to  $C_{1\ 1/2}$  as described above. This represents the harbour concentration; i.e. all outflows have the same concentration.

Lake-harbour exchange<sup>(5, 6)</sup> was included in  $Q_{in}$  and  $Q_{out}$ . Inflow from the lake was assumed to occur to the bottom layer during summer, while outflow from the harbour to the lake was restricted to the top layer. Surface flow to the harbour during summer, as well as flow schemes consisting of more than two layers<sup>(5)</sup> were ignored.

During summer stratification, equation (2) is evaluated separately for each layer, producing concentrations  $C_T$  and  $C_B$  for the top and bottom layer, respectively. All industrial and municipal sources and sinks are assumed to discharge into the top layer.

The equations for determining top and bottom layer COD concentrations are as follows:

$$\frac{dB_T}{dt} = -R_2 B_T + \frac{(\text{load})_T}{V_T} - \frac{E}{d^2} (B_T - B_B) - \frac{W_{S,T}}{d_T} (B_T) + \frac{R_5 A}{V_T} \quad \dots(4)$$

$$\frac{dB_B}{dt} = -R_2 B_B + \frac{(\text{load})_B}{V_B} - \frac{E}{d^2} (B_B - B_T) + \frac{W_{S,T}}{d_T} (B_T) \frac{V_T}{V_B} - \frac{W_{S,B}}{d_B} (B_B) \quad \dots(5)$$

where subscripts T and B refer to top or bottom layers

$W_{S,T}$  and  $W_{S,B}$  = settling velocities from top or bottom layers  
(m day<sup>-1</sup>)

$V_T$  and  $V_B$  = volumes of top and bottom layers (m<sup>3</sup>)

The  $R_5$  term in the top-layer equation is an estimate of internal production of COD by photosynthesis<sup>(9)</sup> and is equal to the rate of oxygen production due to net photosynthesis. No stoichiometric factor is used because BOD is expressed as oxygen equivalents. These equations are solved by dividing by  $B_T$  or  $B_B$  and integrating over  $\Delta t = t_2 - t_1$ , yielding

$$B_{T,2} = B_{T,1} \exp \left[ \left( -R_2 + \frac{(\text{load})_T}{B_{T,1} \frac{1}{2} V_T} - \frac{E(B_T - B_B)}{d^2 B_{T,1} \frac{1}{2}} - \frac{W_{S,T}}{d_T} + \frac{R_5 A}{B_{T,1} \frac{1}{2} V_T} \right) \Delta t \right] \quad \dots(6)$$

$$B_{B,2} = B_{B,1} \exp \left[ \left( -R_2 + \frac{(\text{load})_B}{B_{B,1} \frac{1}{2} V_B} - \frac{E(B_B - B_T)}{d^2 B_{B,1} \frac{1}{2}} + \frac{W_{S,T}}{d_T} \frac{B_{T,1} \frac{1}{2}}{B_{B,1} \frac{1}{2}} \frac{V_T}{V_B} - \frac{W_{S,B}}{d_B} \right) \Delta t \right] \quad \dots(7)$$

Similar to the procedure used with the DO equation, certain terms are approximated at the intermediate time step (1 1/2) for ease of integration. Loading terms for BOD are exactly analogous to those for DO already presented, with the substitution of the appropriate BOD input concentrations.

The equations for NBOD are identical to those for COD, with the substitution of appropriate rate constants, settling velocities, loadings and concentrations. No internal production of NBOD ( $R_5$  term) is assumed. Although internal production of NBOD probably exists, it is neglected in the model due to lack of information on its magnitude.

At each time step, the equations for B and N are first solved, and then the equations for D<sub>0</sub>. The "1 1/2" concentrations are approximated by a two-step procedure in which the equations are first solved using  $C_{1\ 1/2} = C_1$  (or B or N) to obtain an approximate  $C_2$ , which is then averaged with  $C_1$  for a second approximation to  $C_{1\ 1/2}$ . Tests showed that this procedure yielded D.O. curves which were almost independent of time step length  $\Delta t$  for  $\Delta t \leq 0.25$  day.

All rate constants were assumed to be a function of temperature, using expressions

$$R_T = R_{20} \Theta^{(T-20)} \quad \dots(8)$$

where  $R_T$  = any rate constant at temperature  $T^\circ\text{C}$   
 $R_{20}$  = rate constant at  $20^\circ\text{C}$   
 $\Theta$  = temperature coefficient

## MODEL CALIBRATION

### Boundary Conditions

Boundary conditions to the model include the flow rates and concentrations of all industrial, municipal, tributary and nonpoint wastewater sources, as well as exchange with Lake Ontario. The locations of these sources are shown in Figure 1. Data were available as an annual average for 1977<sup>(10)</sup> for the industrial (Stelco and Dofasco) sources; more recent data<sup>(11)</sup> for these sources were incomplete and thus not used. Monthly data for 1979<sup>(11)</sup> were used for the STPs and tributaries; monthly lake-harbour exchange data (B. Kohli, Water Resources Branch, MOE; unpublished) calculated from 1979-1980 current meter results were also used. Stormwater runoff BOD and  $\text{NH}_3$  data<sup>(12)</sup> were available as a modelled 10-year May-October average. Annual averages for all these inputs are given in Table 2. Where available, the actual monthly values were used in the model.

The NBOD values in Table 2 are equal to ammonia concentration multiplied by the factor 4.3. This value is slightly lower than the stoichiometric factor 4.57 for the complete conversion of ammonia to nitrate, and allows for the fact that some ammonia may be utilized by other processes such as photodegradation, volatilization, and assimilation by phytoplankton. On the other hand, additional ammonia may be produced by mineralization of organic nitrogen, which is abundant in Hamilton Harbour. The value 4.3 is the average of several values between 3.9 and 4.5, which were used by other investigators<sup>(13,14,15,16)</sup>.

The model was run for the period March 1 - November 30. Stratified conditions were assumed to exist from May 1 to October 15, with increased vertical diffusion (less stable stratification) before June 30 and after September 1. Initial conditions ( $DO = 13 \text{ mgL}^{-1}$ ,  $BOD = 1 \text{ mgL}^{-1}$ ,  $NH_3 = 2 \text{ mgL}^{-1}$ ) were selected as approximating probable early spring data. The exact values for initial conditions were unimportant as the effect of changing these values rapidly became very small within the first month or two.

#### Chloride Model

The first step in the calibration was a test of the physical portions of the model, by simulating chloride concentration -- a conservative (nonreacting) substance. This allowed a test of the two-layer model formulation, validation (or adjustment) of the hydraulic flow scheme (source inputs, lake-harbour exchange plus convective flow and vertical diffusion between the layers). The input concentrations of chloride used are given in Table 2. No concentration values were available for nonpoint sources, which assume importance in early spring due to runoff contaminated with road salt. A recent study of Toronto area creeks<sup>(17)</sup> showed that most runoff chloride concentrations were 100 to 400  $\text{mgL}^{-1}$ , although values as low as 10 and up to 2000  $\text{mgL}^{-1}$  were recorded. It was found that nonpoint concentrations of 300 and 200  $\text{mgL}^{-1}$  in March and April, respectively, together with an initial condition (February 1980 average) of 69  $\text{mgL}^{-1}$  yielded realistic spring results.



Comparison of observed (1980) and modelled chloride is given in Figure 4. A vertical diffusion coefficient of  $1.0 \text{ m}^2 \text{ day}^{-1}$  ( $= 0.12 \text{ cm}^2 \text{ s}^{-1}$ ) was used. This is lower than the value of  $0.5 \text{ cm}^2 \text{ s}^{-1} = 4.3 \text{ m}^2 \text{ day}^{-1}$  suggested by calculations from vertical oxygen gradients in Hamilton Harbour<sup>(3,4)</sup> and considerably lower than the values of  $4.8$  to  $6.7 \text{ cm}^2 \text{ s}^{-1}$  obtained by Palmer<sup>(18)</sup> from hot film anemometer measurements under stratified conditions. The latter, however, were taken at depths of  $0.5$  to  $3 \text{ m}$  and are, therefore, not representative of thermocline ( $6$ - $9 \text{ m}$ ) conditions. It is somewhat higher than Lake Ontario thermocline values of  $0.02$  to  $0.07 \text{ cm}^2 \text{ s}^{-1}$  obtained by quasi-Lagrangian analysis of vertical heat transport.<sup>(19)</sup> The low vertical diffusion coefficient used in this work was required to simulate the observed epilimnetic and hypolimnetic chloride, concentrations, and their difference, despite the vertical instability of the harbour, which would appear to dictate a higher value. Its value is explored further in sensitivity analyses with the oxygen model.

In order to simulate the observed summer decrease of observed chloride (both layers), it was necessary to increase the July-August exchange flow data from the lake by  $50\%$  above these calculated by B. Kohli. The increase is within the range of values obtained by Snodgrass<sup>(20)</sup> using an exchange flow model based on temperature and dissolved solids. The final exchange rates and vertical diffusion coefficients used in the chloride model were used unchanged in the oxygen model.

#### Oxygen Model Calibration

Measured values for all loading data, as discussed above (Table 2), and certain rate terms such as photosynthesis and sediment oxygen demand were kept fixed. Photosynthesis rates were averages of 1975-1977 data<sup>(21)</sup>. As no significant year-to-year trends existed, it was felt that the averaging process was justified; at any rate, use of a single year's data produced only minor changes in modelled DO. Sediment oxygen demand results were taken directly from measurements by Polak and Haffner<sup>(8)</sup> and Snodgrass<sup>(20)</sup>.

Reaeration rates were calculated as a function of monthly average wind speed from a modification (R. Weiler, pers. comm.) of oxygen transfer coefficients ( $\text{in m s}^{-1}$ ) calculated from laboratory measurements by Banks<sup>(22)</sup> in order to better approximate field conditions. Vertical diffusion and lake-harbour exchange values were kept constant at the values established by the chloride model.

Starting with spring and progressing towards fall, the measured rates of carbon, nitrogen and sulfur oxygen demand already discussed were adjusted on a biweekly to monthly basis until the ammonia, BOD and dissolved oxygen curves derived from the model fitted the measured data averaged over the period 1976 to 1980 as closely as possible. Sulfur demand rates measured by M. Zarull were adjusted by amounts directly proportional to CBOD to avoid excessive DO depletion rates during early spring and fall. In choosing the rates, greatest weight were placed on minimizing the difference between the measured and calculated oxygen curves. Final fine tuning was done by adjusting the settling rates for carbon and nitrogen. Once these rates, which were assumed to be independent of concentrations but dependent upon the season, were established, the model was considered to be calibrated.

The calibrated rates are given in Table 3. Included in this table also are photosynthesis and reaeration rates as described above. Temperature dependence of these constants and the sulfur demand rate were included in the seasonal variation. Vertical sinking velocities for CBOD and NBOD are also given in Table 3.

## RESULTS

Figure 5A - 5F compare the predicted and observed (1976-1980) concentrations in the harbour. For most of the year, the model results reproduce the observed DO and NBOD curves satisfactorily. The underestimate of NBOD in early spring, and the low decay coefficients in this time period (Table 3) may be due to the lack of



an NBOD production term in the model equation. The error limits ( $\pm 2$  standard errors of the mean) include both between-year and spatial variabilities and are higher in the epilimnion than in the hypolimnion for most sampling intervals.

Deviations of the model CBOD curve from the average (1976-80) curve are greater. No combination of rate constants was able to fit the spring data to the observed curve without an excessive rate of DO decline before the end of April. In addition, the BOD measurements on the harbour water are not directly comparable to those on the wastewater loads. The harbour BODs were 5-day total water column oxygen depletion rates without dilution, nutrient spike or seed, and undoubtedly contained a nitrification component (which was probably most significant during the June-July period of rapid nitrification). On the other hand, the measurements done on the effluents were proper BOD measurements and should represent true carbonaceous values. Therefore, the observed and modelled BOD (Figures 5c,d) cannot be strictly compared and no improvement in the difference between these curves was sought.

Model validity was also checked by doing linear regression of observed vs. model data for both layers. Ideally, such a regression should yield a straight line with a slope of one and an intercept of zero. Using a t-test at the 95% level of confidence, the slope and intercept of the regression for D.O. were not significantly different from the expected values. The coefficient of determination ( $r^2$ ) was 0.67 for the surface layer and 0.89 for the bottom layer. In the case of NBOD, the slope was significantly greater than one and the intercept significantly less than zero, because of the spring underestimate of NBOD already described. If data before mid-June are deleted, the regression coefficients produce an improved fit to the expected values, with  $r^2 = 0.59$  for the surface layer and 0.65 for the bottom layer. The CBOD regression produced low  $r^2$  values (0.03, surface and 0.09, bottom) due to the measurement problems already described.

### Sensitivity Analyses

In order to test the relative effect of various terms on the dissolved oxygen values, sensitivity analyses were performed. For many parameters, this involved increases or decreases of 50% from the value used in the calibration. For reaeration, equations supplied by different authors<sup>(13,22,23,24)</sup> were substituted. These equations were all nonlinear functions of the average wind speed. Reaeration (Figure 6a-b) had by far the greatest effect on surface DO of any parameter studied, and also had a substantial effect on hypolimnetic dissolved oxygen through the vertical diffusion term. Other parameters had only very small effects on surface dissolved oxygen (Figures 7a-11a). The hypolimnetic dissolved oxygen was most sensitive to the values of vertical diffusion (Figure 7b), lake-harbour exchange (Figure 8b), reaeration (Figure 6B), vertical settling (Figure 10b), stratification depth (Figure 9b), and photosynthesis (Figure 11b), in that order. Stratification depth (Figure 9) was varied through 6-9 m, a realistic range for the harbour. The effect of photosynthesis (Figure 11a-b) on dissolved oxygen was minor, because of a feedback effect from increased internal BOD production accompanying increased oxygen production. Both vertical settling and photosynthesis had strong effects on the value of modelled BOD, and vertical settling was significant for modelled nitrogen.

### DISCUSSION

The results presented here represent a calibration of a dissolved oxygen model for Hamilton Harbour. Ideally, such a model should be verified before it is used for predictive purposes by applying the same set of coefficients to a different set of input data and obtaining model results in realistic agreement with the observed. However, verification has not been possible for two reasons: first, the harbour dissolved oxygen does not differ much from one year to another, and second, no complete input data set exists for individual years. Indeed, the data in use is a composite of several years. If future reduced loadings of oxygen-demanding substances produced increased DO in agreement with model estimates, this could serve as a verification.

The most important limitation in the model is that not all known processes which add or subtract CBOD or NBOD are included because the magnitudes of the inputs or rates are unknown. Instead, sources such as internal production of ammonia from particulate nitrogen, and sinks such as the uptake of ammonia by phytoplankton or its escape to the atmosphere, are included in the loading of ammonia from external sources and their removal by nitrification and sinking to the sediments. Therefore, the rate constants in Table 3 are empirical and differ from the measured rates in Table 2.

The rates of these oxygen demanding processes are known to be dependent upon the time-varying bacterial populations such as nitrifiers and sulfur oxidizers. These processes are inhibited at reduced oxygen concentrations as found in the hypolimnion during mid-summer. The combined effects of these assumptions are represented by letting the deoxygenation rate constants at 20°C vary seasonally over periods of 1/2 to 1 month during the simulation.

The calibrated model can be used to improve the older estimates<sup>(3)</sup> of the contributions of the various sources and sinks to the harbour dissolved oxygen stock, by calculation of values for the individual rate terms in equation (2). Percentage contributions of various oxygen sources, averaged over intervals of relatively constant contributions, are given in Table 4. As noted previously, reaeration is the most important source of oxygen to the harbour during summer and fall. Although reaeration was also the largest oxygen source during spring, other sources (lake-harbour exchange, photosynthesis, and tributaries and discharges) contributed almost as much as reaeration. The relative contribution in Table 4 should be more realistic than those of Polak and Haffner (8), as reaeration is calculated rather than being obtained by difference and also included inputs from outfalls and tributaries. The importance of reaeration is reduced in early spring because the surface waters of the harbour are only slightly undersaturated.

Estimates of DO losses (not including oxygen in water physically removed into Lake Ontario) indicate that during spring, WCOD (including carbonaceous, nitrogenous and sulfurous demands) represents about 60%, and SOD about 40% of losses. Throughout the summer and fall, WCOD predominates (as suggested by earlier studies), accounting for 80-90% of total oxygen demands in summer, and about 75% in fall. The shift in importance is caused by the declining dominance of SOD as the hypolimnetic DO concentration drops, at the same time that the bacterial populations controlling WCOD are growing rapidly.

#### SUMMARY AND CONCLUSIONS

1. A two-layer, horizontally well-mixed model of dissolved oxygen in Hamilton Harbour has been developed. Oxygen sources include photosynthesis, reaeration and mass exchange with Lake Ontario. Oxygen demanding processes include water column biochemical oxygen demand (carbonaceous, nitrogenous and sulfurous) and sediment oxygen demand. Terms for input of oxygen demanding substances from industrial, municipal, tributary and non-point sources have been included in the model, as well as exchange between the layers and settling of particulate oxygen-demanding materials.
2. The physical portions of the model were calibrated by simulating the seasonal variations of chloride, a nonreacting substance. This assisted in establishing values for the vertical diffusion between the layers, and confirming the lake-harbour mass exchange.
3. The biochemical portion of the model was calibrated by adjusting the measured water column decay rates until reasonable agreement between observed and computed dissolved oxygen, BOD and ammonia data were obtained. The agreement between measured and modelled CBOD was limited by the nature of experimental measurements of harbour BOD.

4. Sensitivity analyses showed that the modelled hypolimnetic dissolved oxygen was most sensitive to the input values of vertical diffusion, lake-harbour exchange, reaeration, vertical settling of particulates, stratification depth, and photosynthesis in that order. Epilimnetic dissolved oxygen was sensitive to the reaeration value only.
5. The main limitation to the calibrated model is the difficulty of simulating internal processes affecting BOD and ammonia, and the effect of bacterial populations on these processes. Other limitations involve establishing the values for photosynthesis, reaeration, lake-harbour exchange and sediment oxygen demand.

Despite these limitations, it is hoped that this model will prove useful in predicting the amount of reduction of oxygen-demanding inputs required in order for the harbour dissolved oxygen to reach Provincial objectives. As abatement procedures are implemented, concentrations of dissolved oxygen and oxygen-demanding substances should be monitored, and further research should be undertaken in order to quantify better all important processes such as internal oxygen demand loadings, photosynthesis, reaeration and sediment oxygen demand and its rate of decay. This would improve the confidence in the model and its predictive capabilities.

#### ACKNOWLEDGEMENTS

Many people associated with the Great Lakes Section participated in the preparation of this paper. In particular, I would like to thank Dr. M.A. Zarull, who performed the experiments on water column oxygen demand and who, along with Dr. R. Weiler and Dr. B. McGillvray, provided numerous helpful comments on the manuscript. Much of the computer programming was done by M. Lau and W. Adams, while L. Senyshyn performed the difficult task of programming the plotter routines used to prepare most of the figures.

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TABLE 1

## EXPERIMENTALLY MEASURED DEOXYGENATION RATE CONSTANTS

Month (1980)	Ambient Temperature (°C)	$R_2$ (day <sup>-1</sup> ) (CBOD)			$R_3$ (day <sup>-1</sup> ) (NBOD)			$R_4$ (mgO <sub>2</sub> L <sup>-1</sup> day <sup>-1</sup> ) (sulfur) Measured
		Meas.	$\theta$	Corrected to 20°C	Meas.	$\theta$	Corrected to 20°C	
Jan. - Feb.	4	0.05	1.05	0.11	0.006	1.09	0.03	0.25
Mar. - Apr.	7.8	0.04	1.05	0.07	0.011	1.09	0.03	0.24
May - June	10.9	0.06	1.05	0.10	0.04	1.09	0.11	0.22
July - Aug.	14.5	0.07	1.05	0.09	0.13	1.09	0.21	0.11
Sept. - Oct.	16.8	0.24	1.05	0.28	0.43	1.09	0.57	0.35

Note:  $\theta$  values from  $R_2$  and  $R_3$  were taken from average literature values (13).

$R_4$  was not corrected for temperature as  $\theta$  values were not available.

TABLE 2

AVERAGE INPUT FLOWS AND CONCENTRATIONS HAMILTON HARBOUR MODEL

Source	Map Location	Flow $10^3 \text{ m}^3 \text{ d}^{-1}$	$\text{Cl}^-$	DO ( $\text{mg L}^{-1}$ )	CBOD	NBOD
Hamilton STP*	A1	247	158	8 <sup>+</sup>	37	83
Stelco Ottawa St	B1	446	63	10 <sup>+</sup>	10	1.3
Dofasco Ottawa St	B2	208	97	10 <sup>+</sup>	27	23
Stelco WSO	D	218	83	10 <sup>+</sup>	3.2	22
" NWD	E	273	70	10 <sup>+</sup>	3.8	64
" #30H	G	237	65	10 <sup>+</sup>	4.0	1.7
" 148" Plate	H	73	63	10 <sup>+</sup>	10	1.3
Stelco and Dofasco Intakes	C+F+I	-2014	-	-	-	-
Dofasco Kenilworth St	J	551	71	10 <sup>+</sup>	17	32
Burlington STP*	K	77	100	8 <sup>+</sup>	19	6.5
Cootes Paradise*	L	96	49	9.6	4.5	0.9
Grindstone Creek*	M	50	139	13	1.2	0.4
Red Hill Creek*	A2	58	121	10 <sup>+</sup>	2.6	5.3
Nonpoint Sources	-	92**	50 <sup>+</sup>	10 <sup>+</sup>	24 <sup>++</sup>	31 <sup>++</sup>
Lake Ontario inflow*	N	2500**	28	12	0	0

Note: Except where indicated, 1977 average values were used (10).

\* Values indicated are March-November 1979 averages (11).

+ Assumed value. Assumed values for March and April  $\text{Cl}^-$  were 300 and 200  $\text{mg L}^{-1}$ , respectively.

++ Averaged values from Robinson and James (12).

\*\* Average of 1979-1980 values (B. Kohli, unpublished data).  
Actual monthly values were used in model.

TABLE 3

Values of Calibrated Model  
Rate Constants (20°C)

Date	$R_1$ ( $d^{-1}$ )	$R_2$ ( $d^{-1}$ )	$R_3$ ( $d^{-1}$ )	$R_4$ ( $gO_2m^{-3}d^{-1}$ )	$R_5$ ( $gO_2m^{-2}d^{-1}$ )
	Reaeration	CBOD decay	NBOD decay	SBOD decay	Net photosynthesis
March	0.27	0.03	0.002	0.08	0.6
April	0.24	0.03	0.002	0.08	0.9
May 1-15	0.41	0.03	0.005	0.08	1.1
May 16-31	0.41	0.035	0.01	0.08	1.1
June	0.36	0.045	0.04	0.11	1.1
July	0.38	0.055	0.07	0.07	1.45
August	0.37	0.06	0.10	0.07	1.4
September	0.39	0.093	0.15	0.12	1.2
October 1-15	0.37	0.093	0.15	0.12	0.75
October 16-31	0.25	0.08	0.15	0.10	0.75
November	0.25	0.056	0.15	0.07	0.7

Temperature coefficients  $\theta_1 = \theta_4 = \theta_5 = 1.0$   
 $\theta_2 = 1.05$   
 $\theta_3 = 1.09$

Settling rates: Epilimnetic BOD =  $0.15 \text{ m day}^{-1}$  (May, June)  
 $0.25 \text{ m day}^{-1}$  (July-Oct.)  
Hypolimnetic BOD =  $0.05 \text{ m day}^{-1}$  (May, June)  
 $0.10 \text{ m day}^{-1}$  (July-Oct.)  
Epilimnetic NOD =  $0.10 \text{ m day}^{-1}$  (May, June)  
 $0.15 \text{ m day}^{-1}$  (July-Oct.)  
Hypolimnetic NOD =  $0.01 \text{ m day}^{-1}$

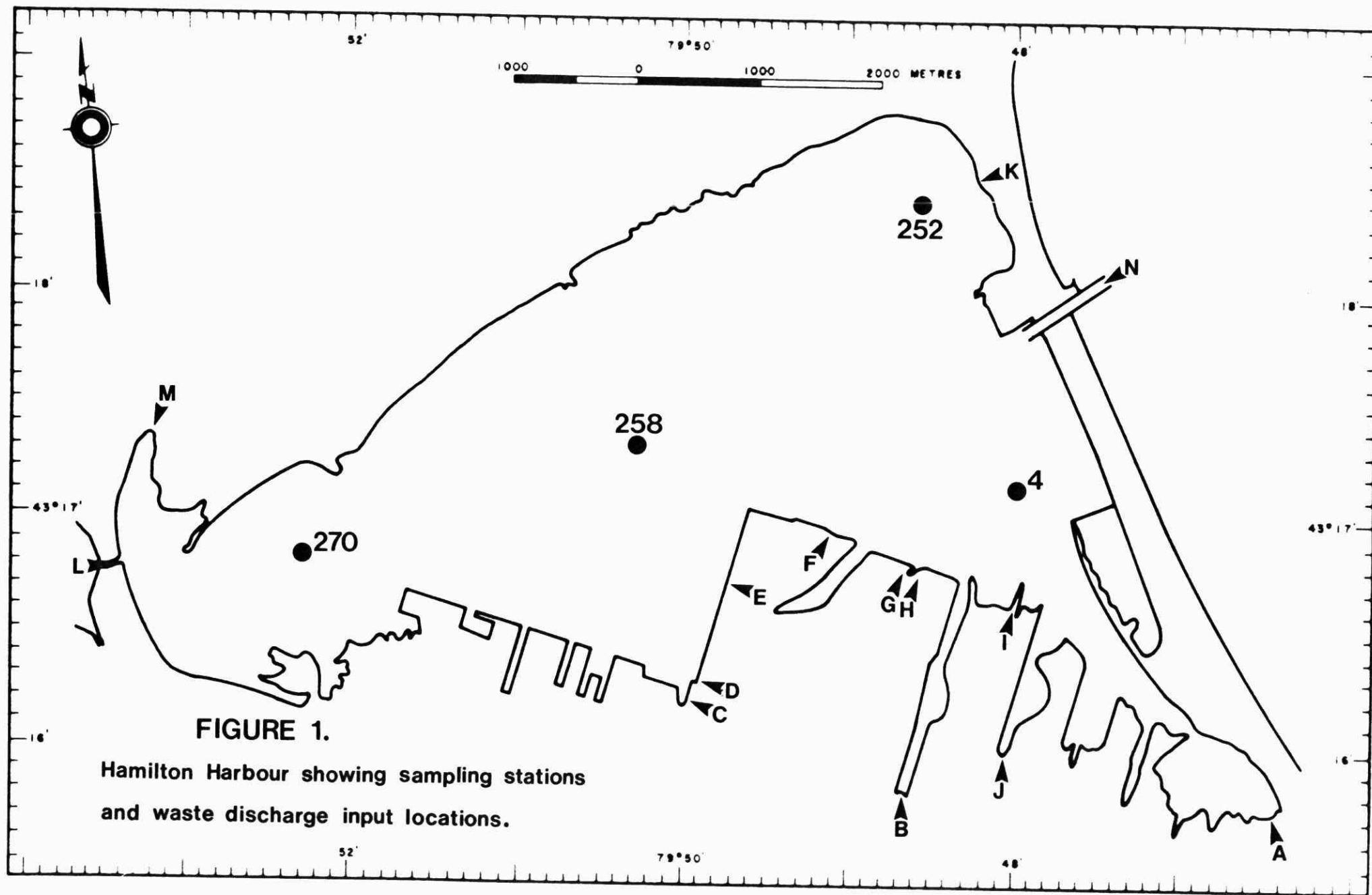
Vertical diffusion ( $E$ ) =  $1 \text{ m}^2 \text{ day}^{-1}$  from July 1 to August 31.  
Linear decrease from  $50 \text{ m}^2 \text{ day}^{-1}$  during May and June, and linear increase to  $20 \text{ m}^2 \text{ day}^{-1}$  during September and October.

TABLE 4

CONTRIBUTION OF VARIOUS SOURCES TO  
HAMILTON HARBOUR DISSOLVED OXYGEN BUDGET,  
CALCULATED FROM MODEL DATA

Season	Reaeration	Lake- Harbour Exchange	Photo- synthesis	Tributaries and Discharges
Spring (March-May)	32	26	18	24
Summer (June -Sept.)	55	16	16	13
Fall (Oct. -Nov.)	66	15	7	12

Numbers are percentage of total dissolved oxygen input to the harbour  
from the indicated source.



**FIGURE 1.**

Hamilton Harbour showing sampling stations  
and waste discharge input locations.

FIGURE 2a. EPIILIMNETIC DISSOLVED OXYGEN CONCENTRATIONS  
AT STATIONS 4, 258 & 270 IN 1976

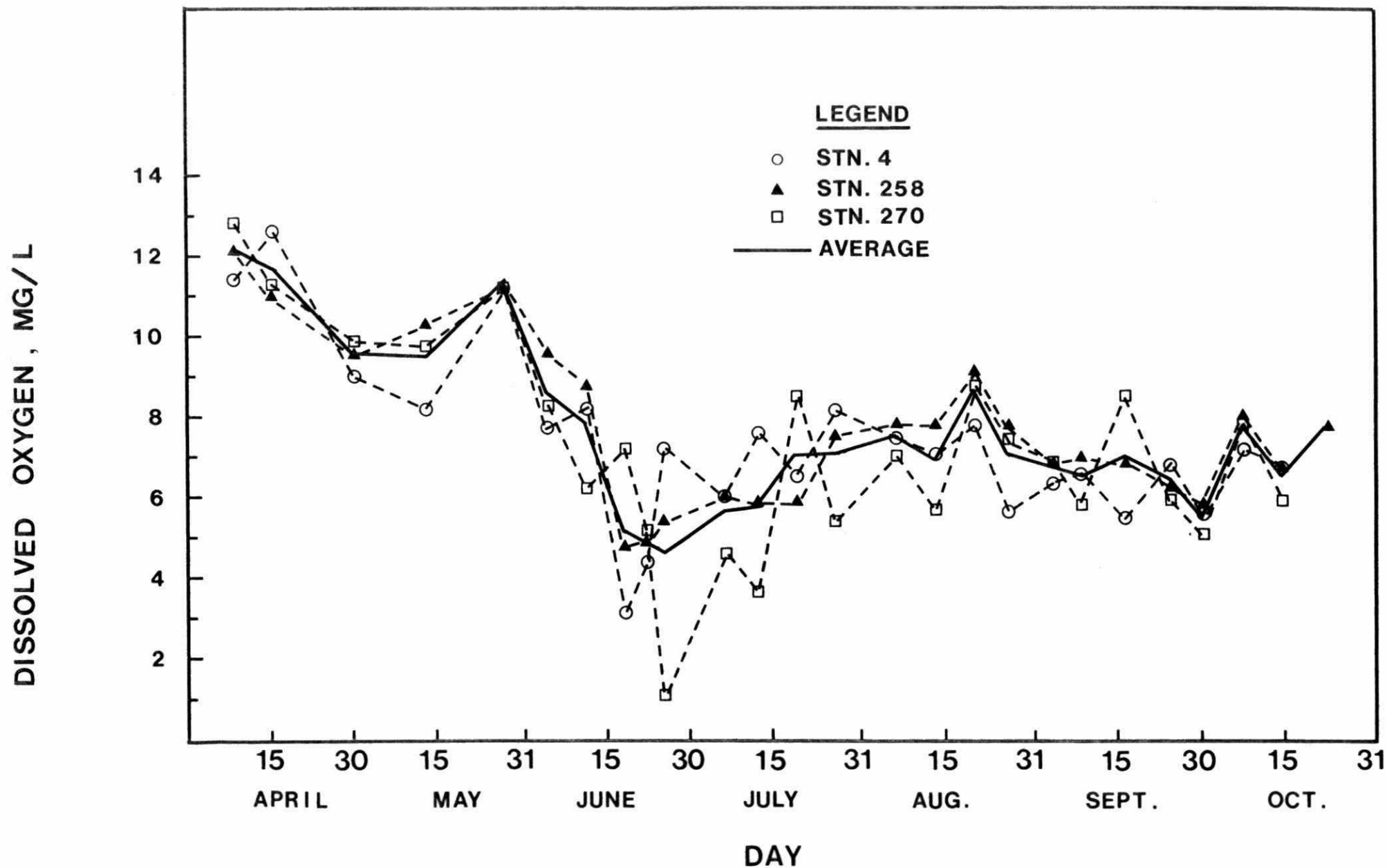
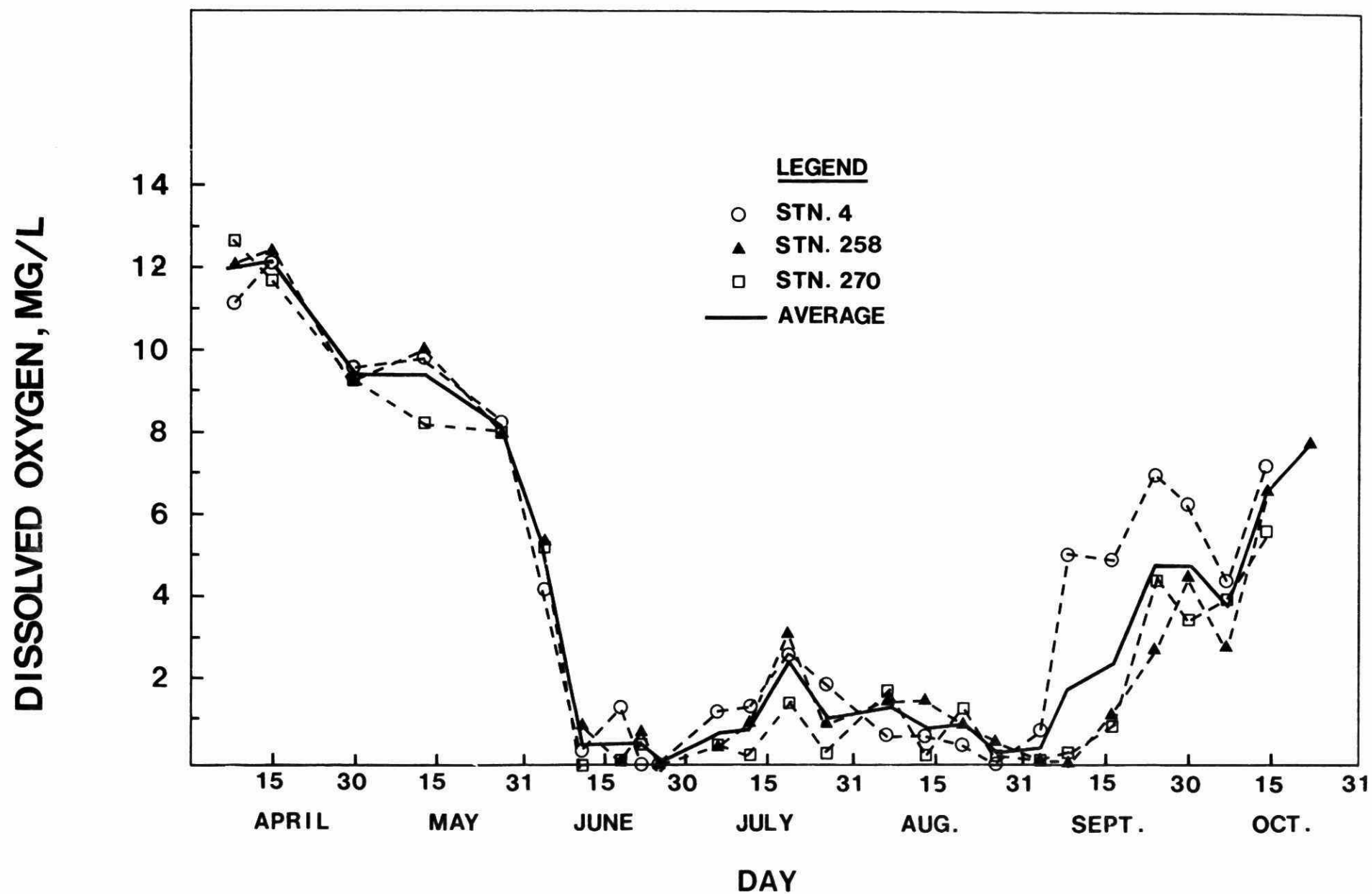


FIGURE 2b. HYPOLIMNETIC DISSOLVED OXYGEN CONCENTRATIONS  
AT STATIONS 4, 258 & 270 IN 1976.



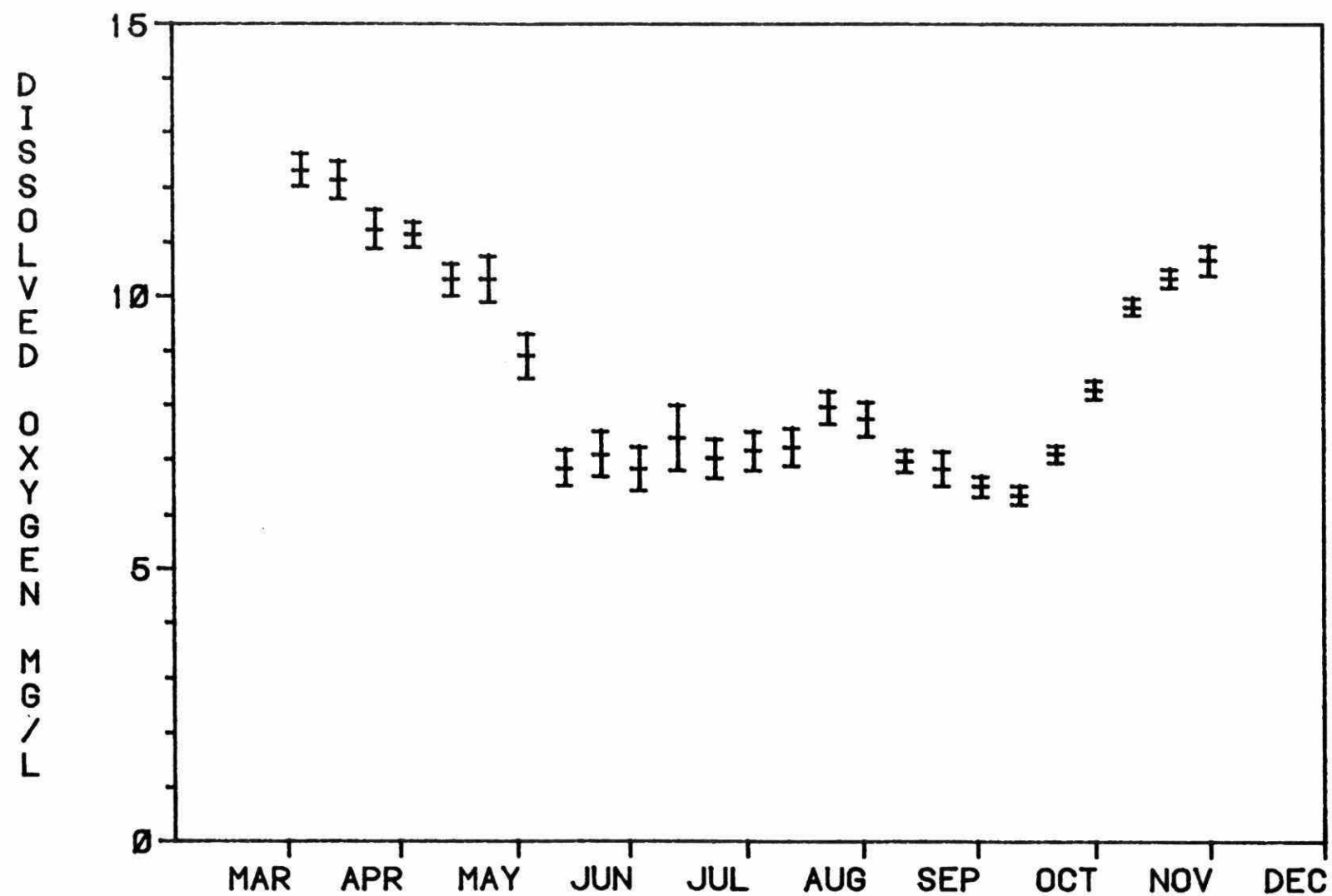


Fig. 3A. DISSOLVED OXYGEN 10-DAY MEANS (1976-80)  
FOR THE TOP LAYER OF HAMILTON HARBOUR



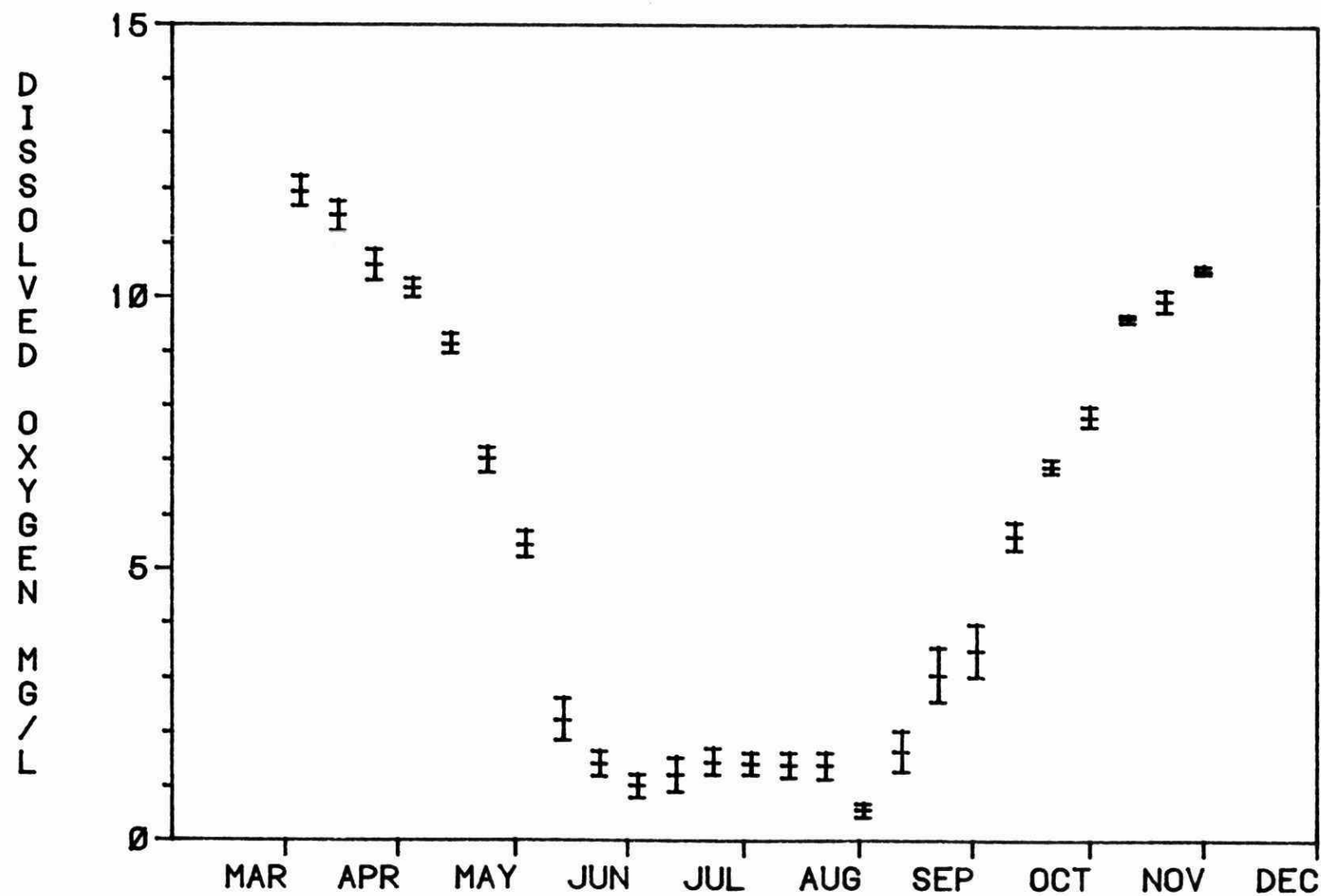


Fig. 3B. DISSOLVED OXYGEN 10-DAY MEANS (1976-80)  
FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

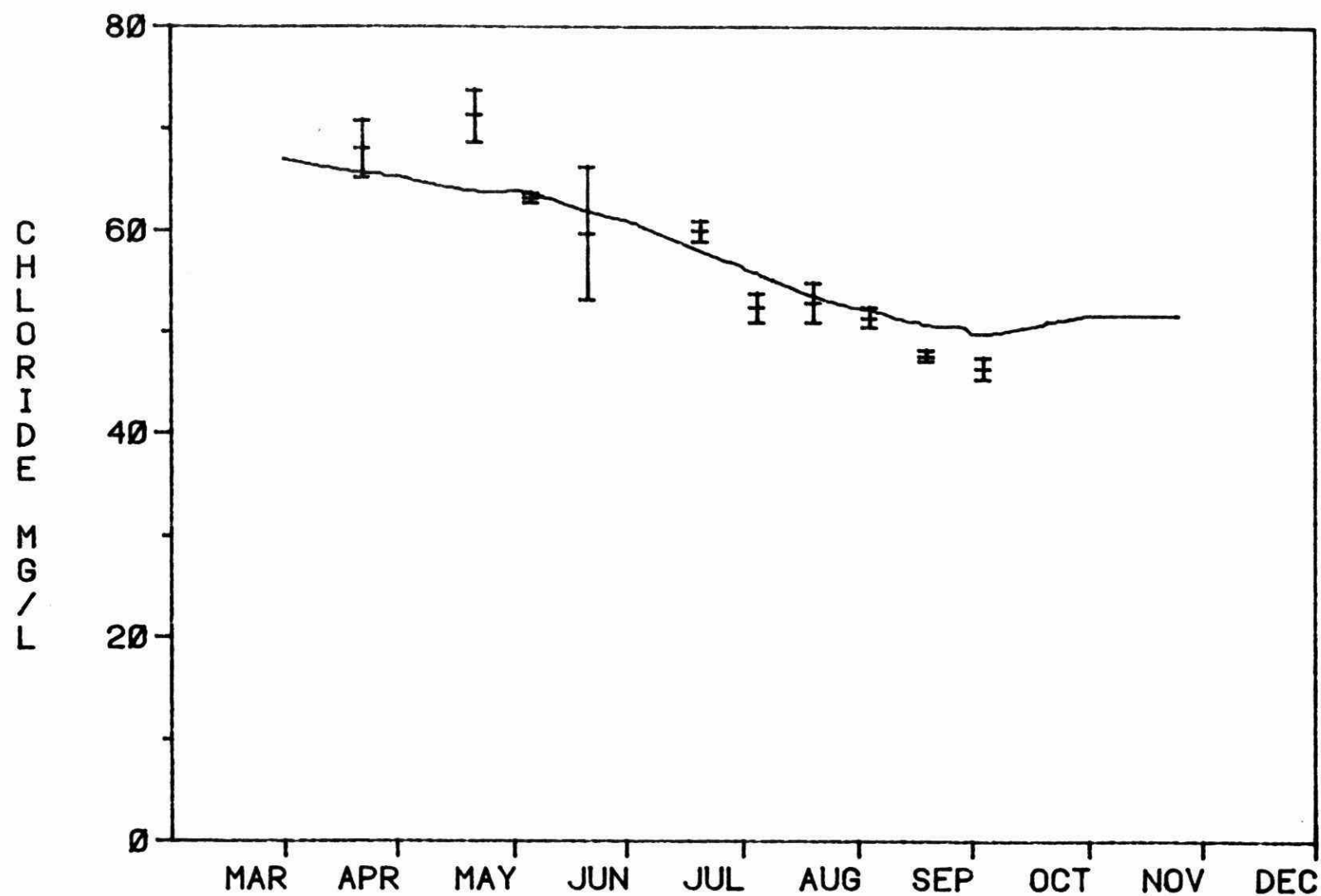


Fig. 4A. Predicted and observed concentrations of chloride for the top layer of Hamilton Harbour.

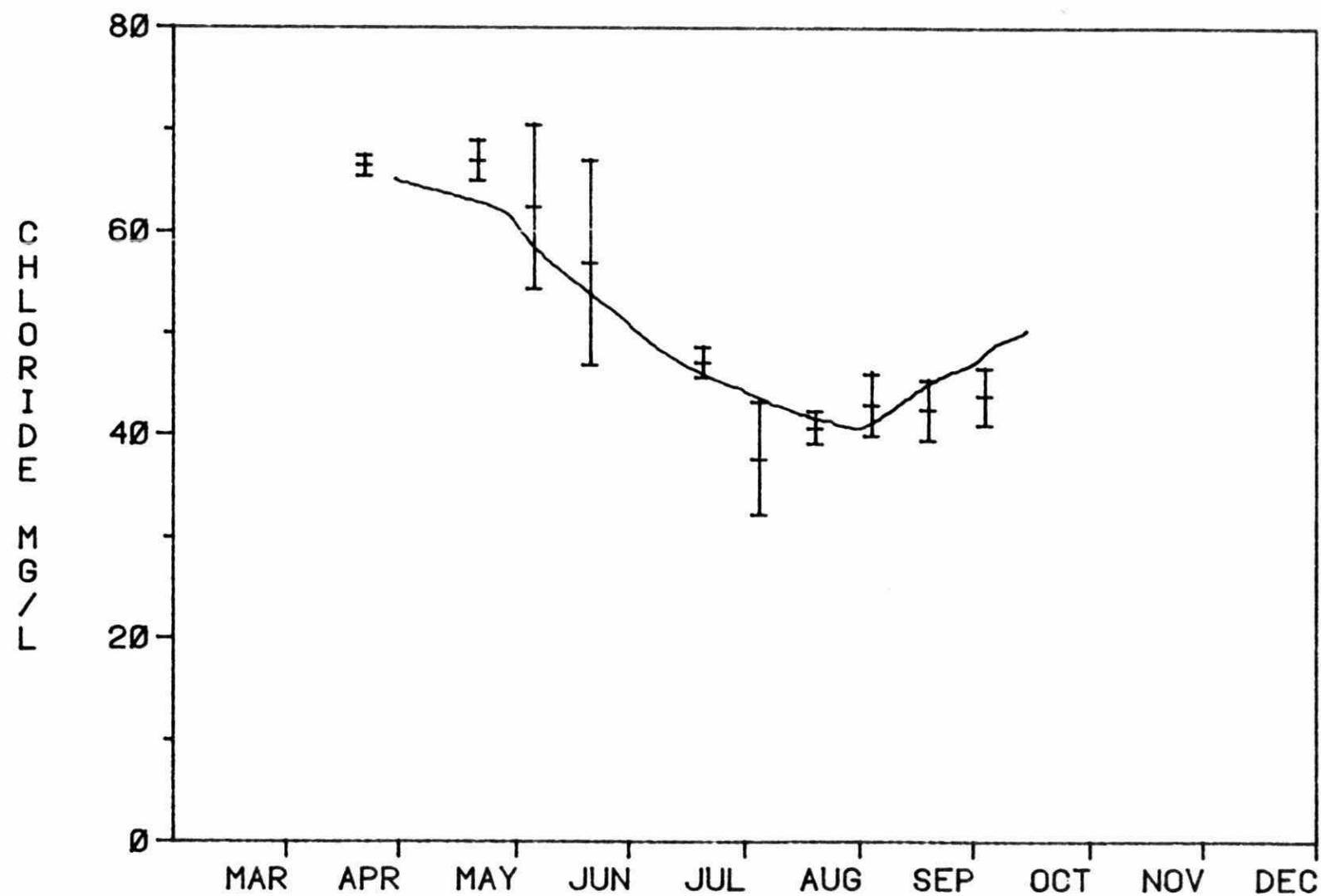


Fig. 4B. Predicted and observed concentrations of chloride for the bottom layer of Hamilton Harbour.

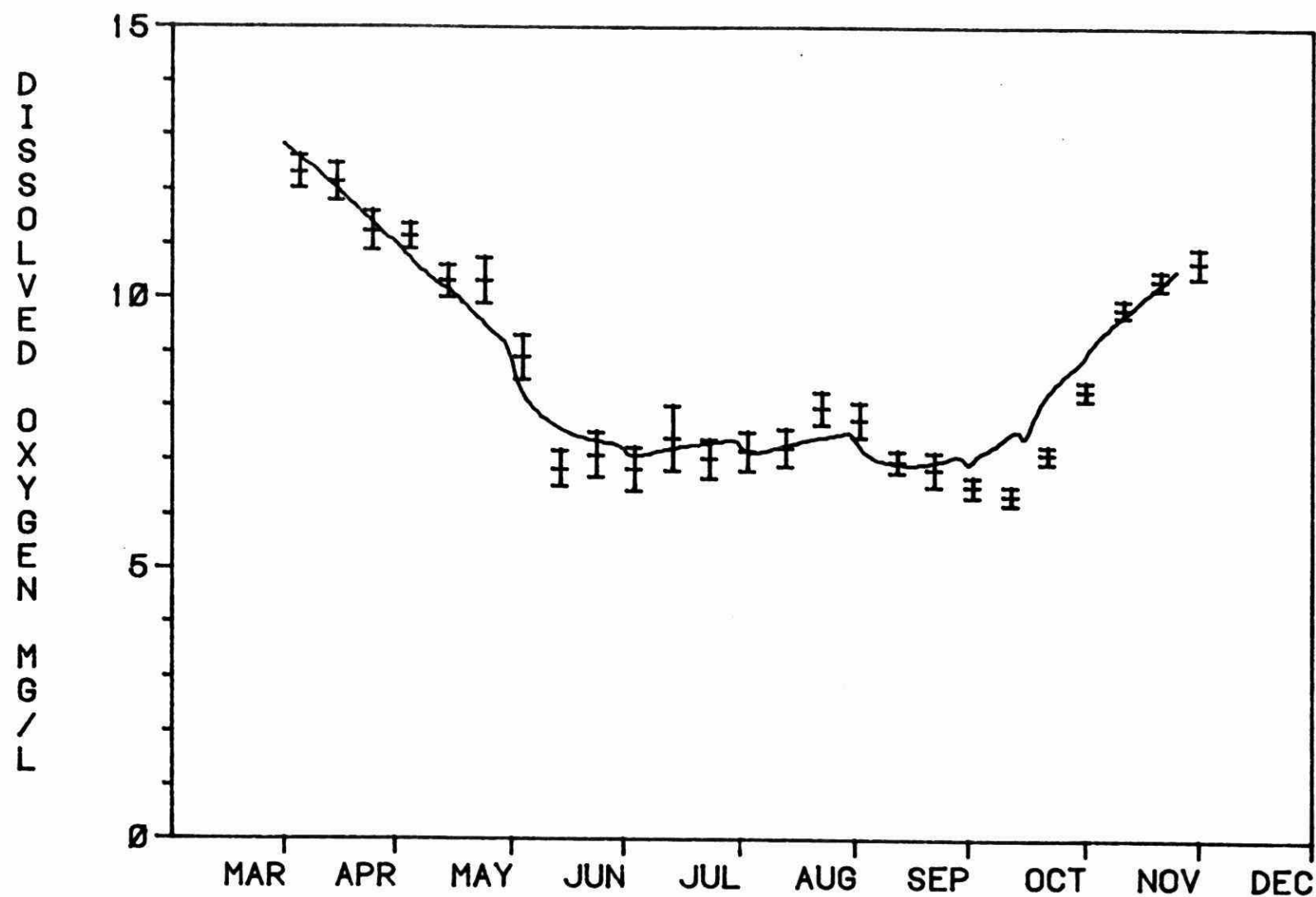


Fig. 5A. Predicted and observed concentrations of dissolved oxygen for the top layer of Hamilton Harbour.

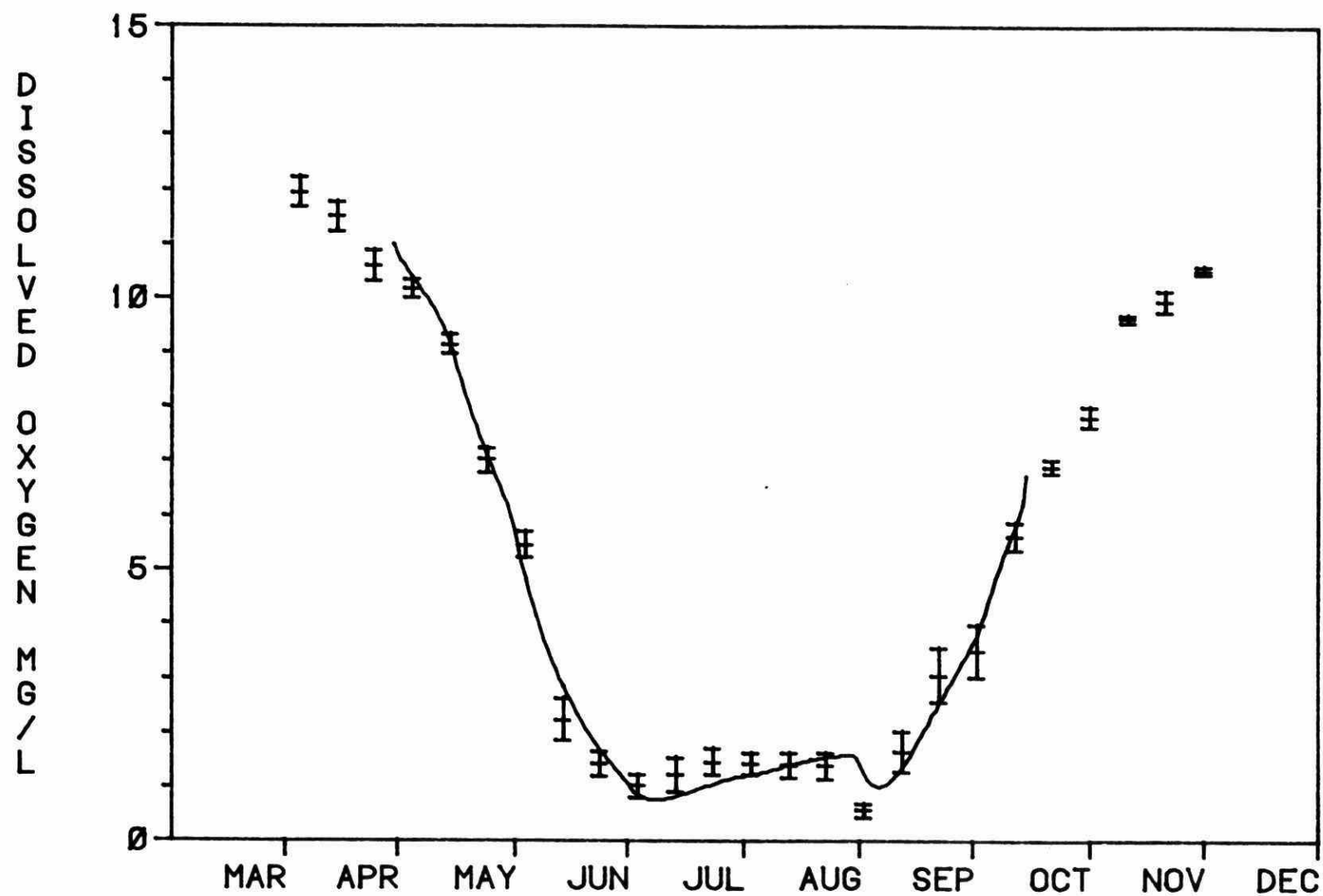


Fig. 5B. Predicted and observed concentrations of dissolved oxygen for the bottom layer of Hamilton Harbour.

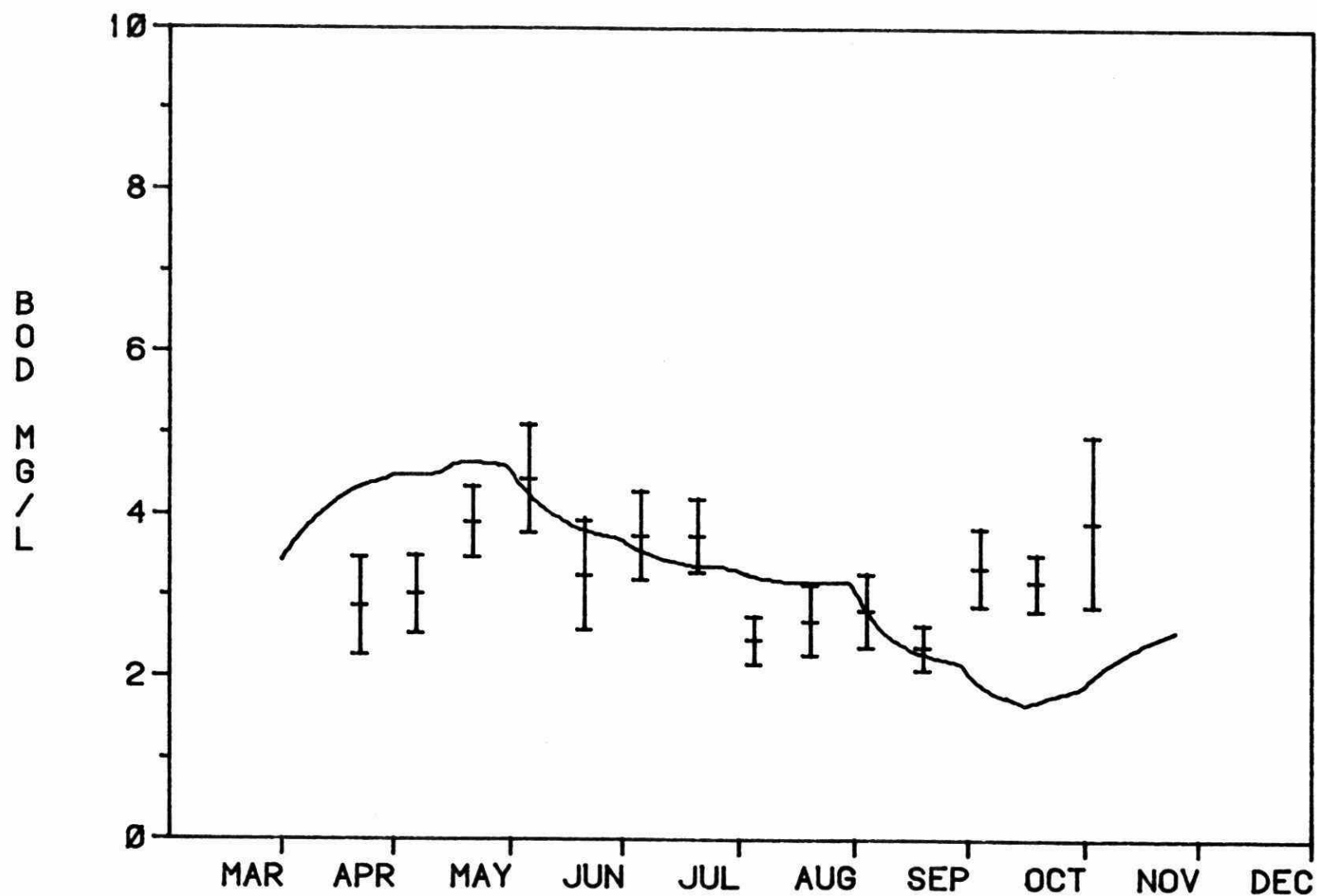


Fig. 5C. Predicted and observed concentrations of BOD for the top layer of Hamilton Harbour.

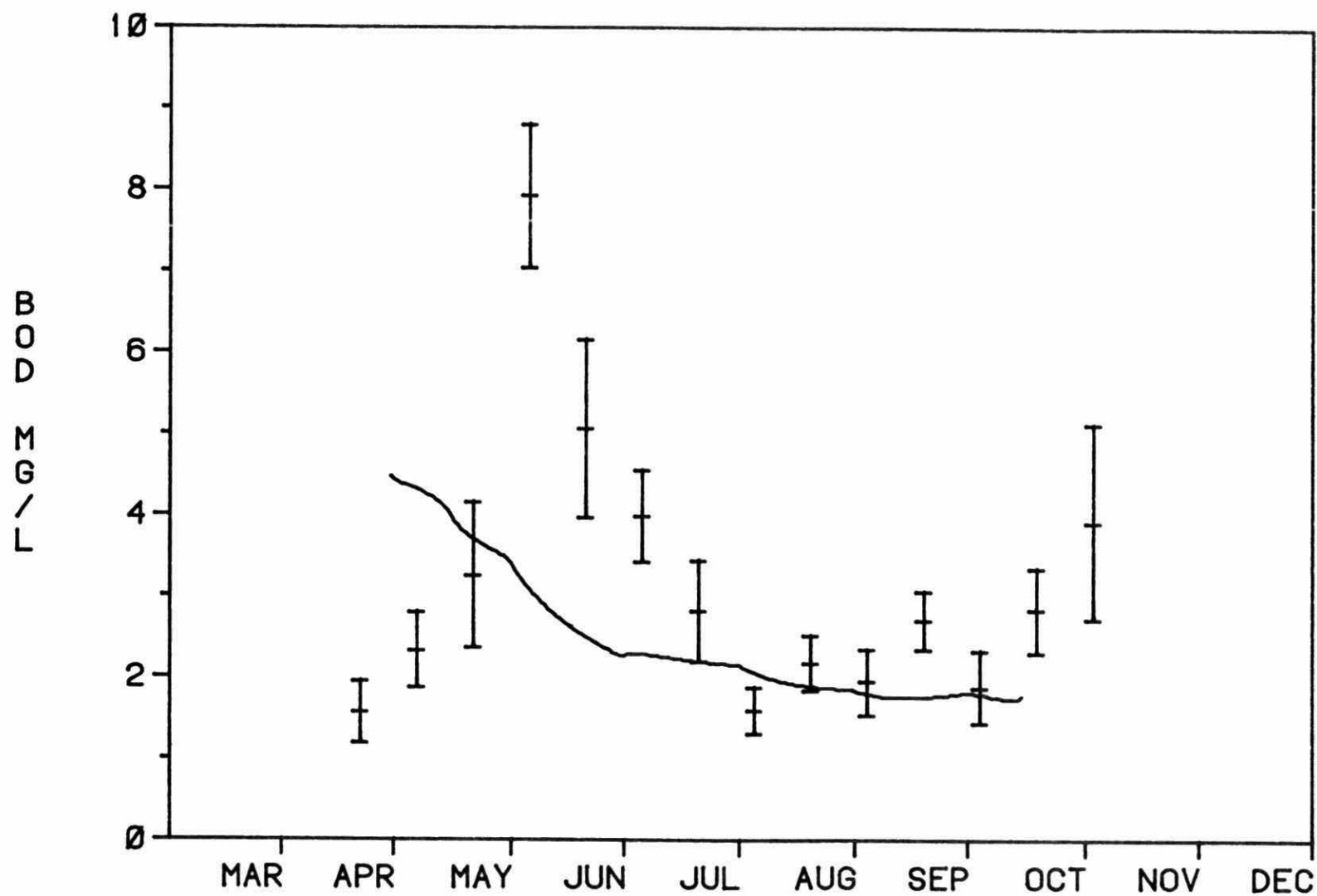


Fig. 5D. Predicted and observed concentrations of BOD for the bottom layer of Hamilton Harbour.

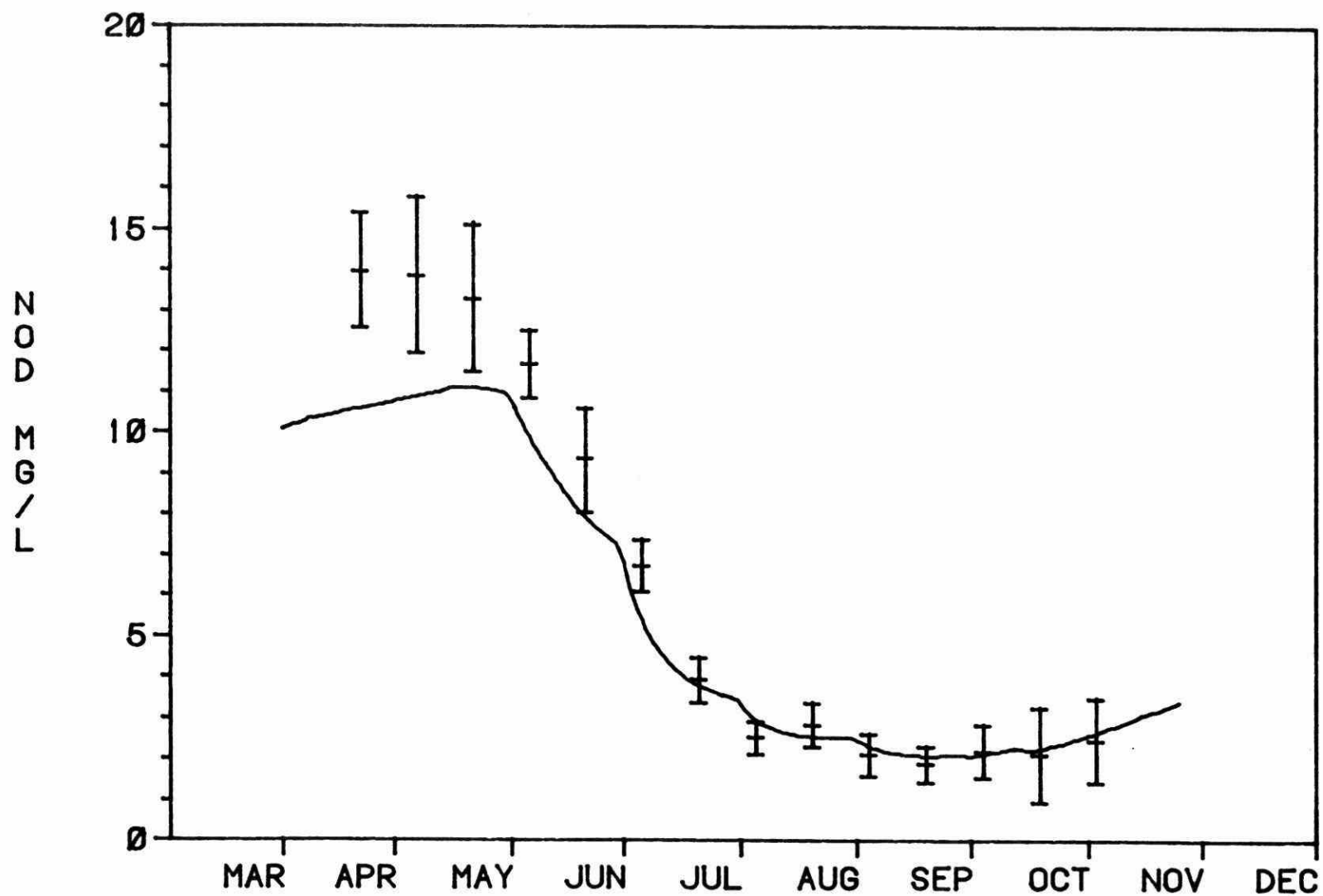


Fig. 5E. Predicted and observed concentrations of NOD for the top layer of Hamilton Harbour.



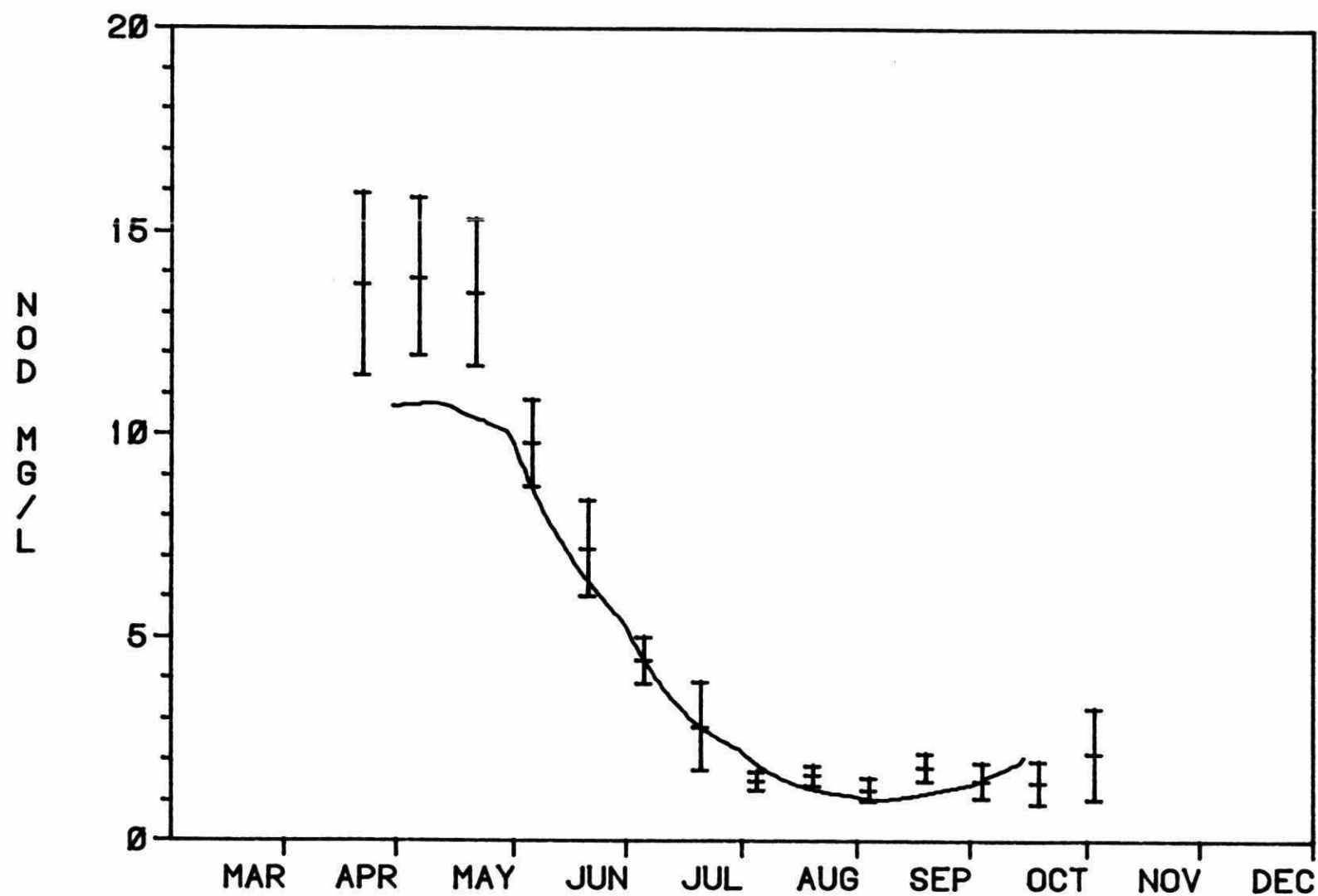


Fig. 5F. Predicted and observed concentrations of NOD for the bottom layer of Hamilton Harbour.

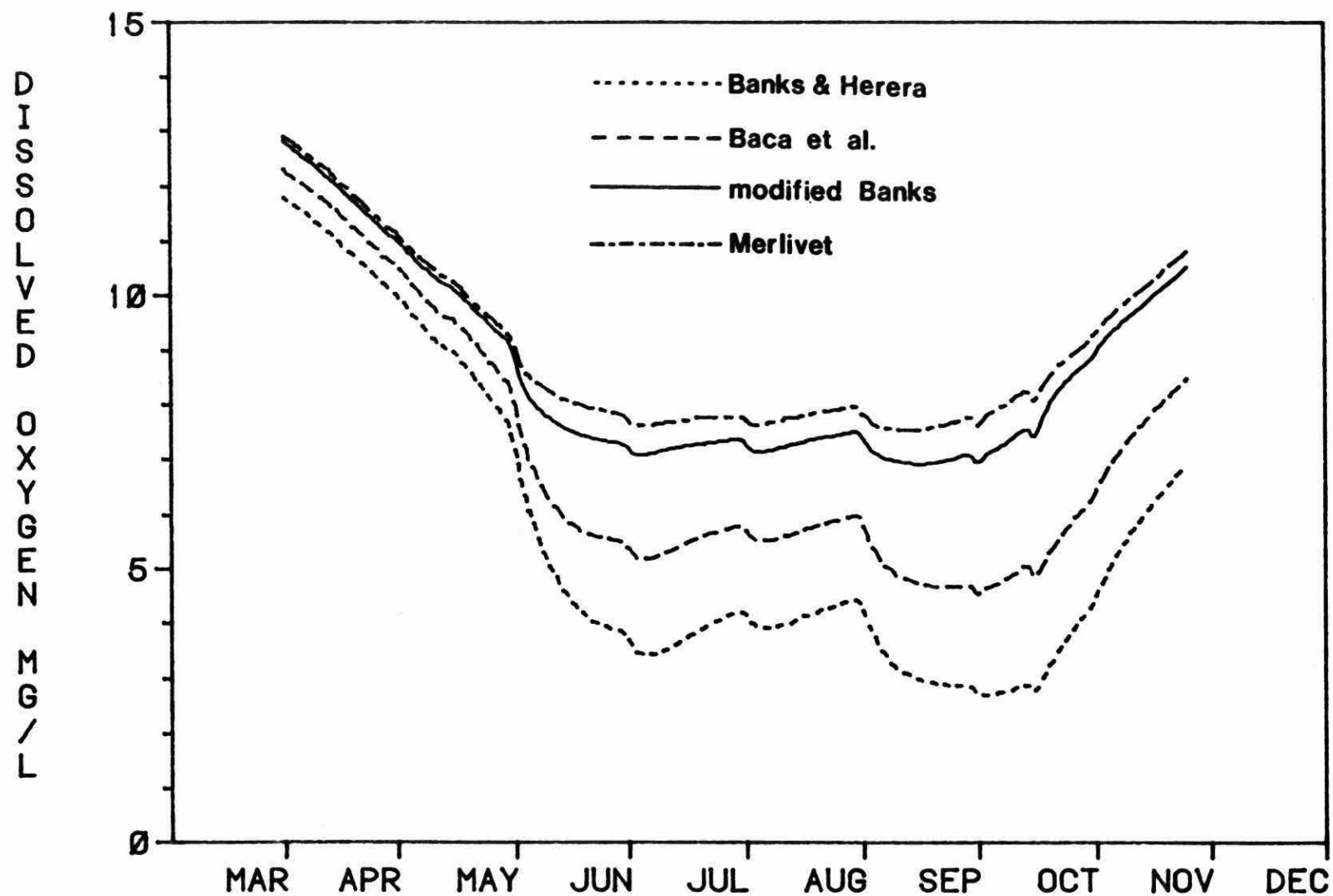


FIG. 6A. EFFECT OF REAERATION ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.

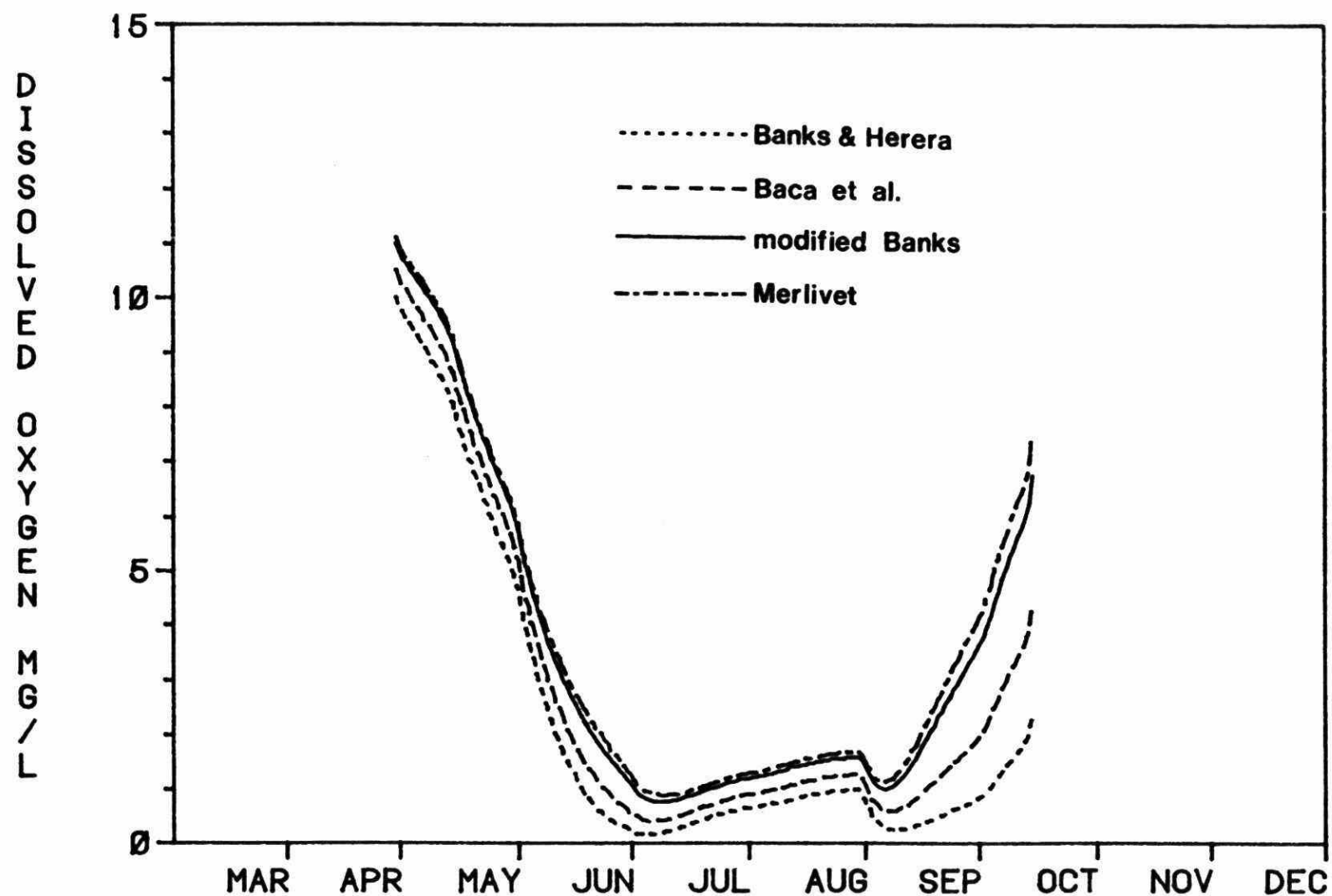


FIG. 6B. EFFECT OF REAERATION ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

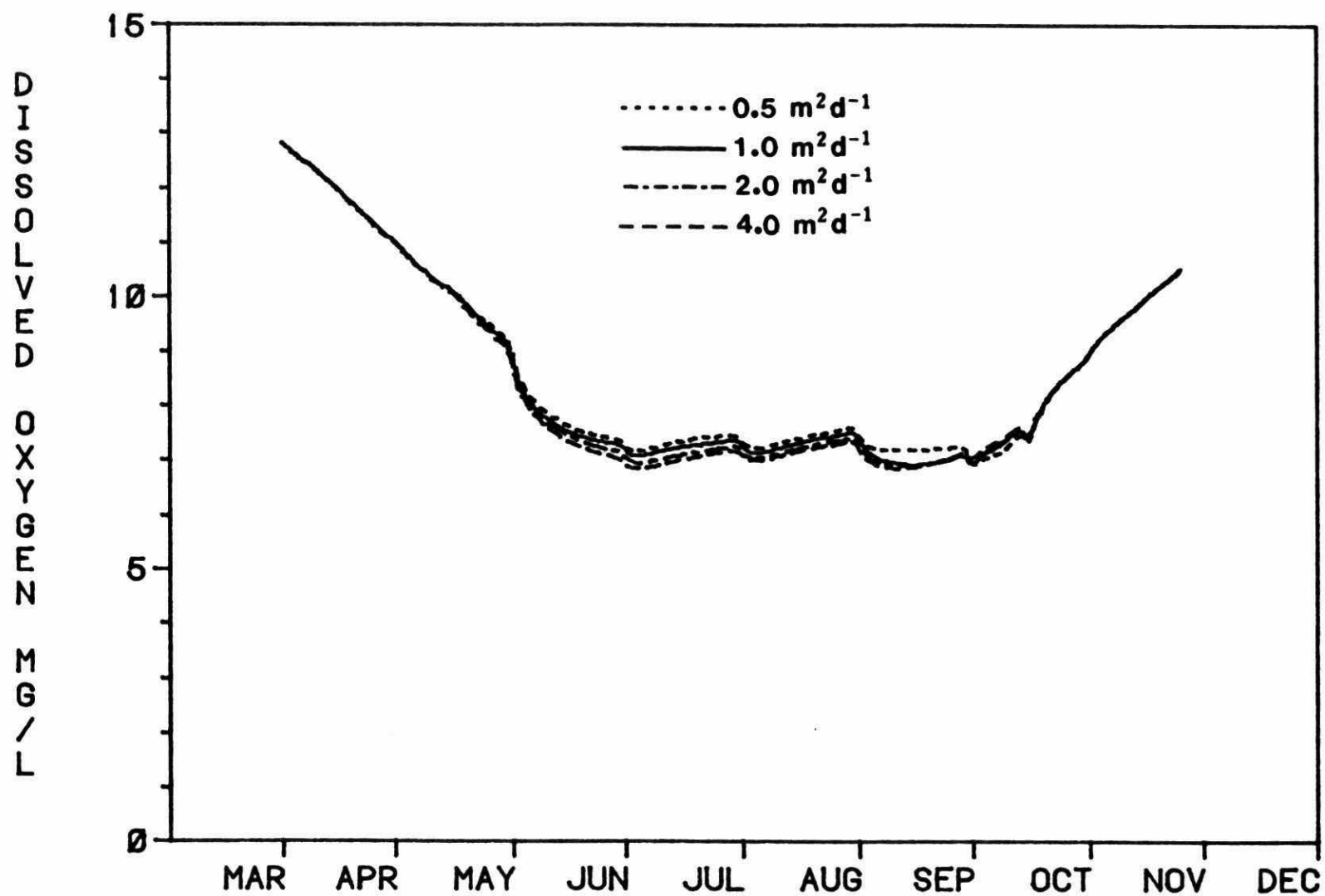


FIG. 7A. EFFECT OF VERTICAL DIFFUSION ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.

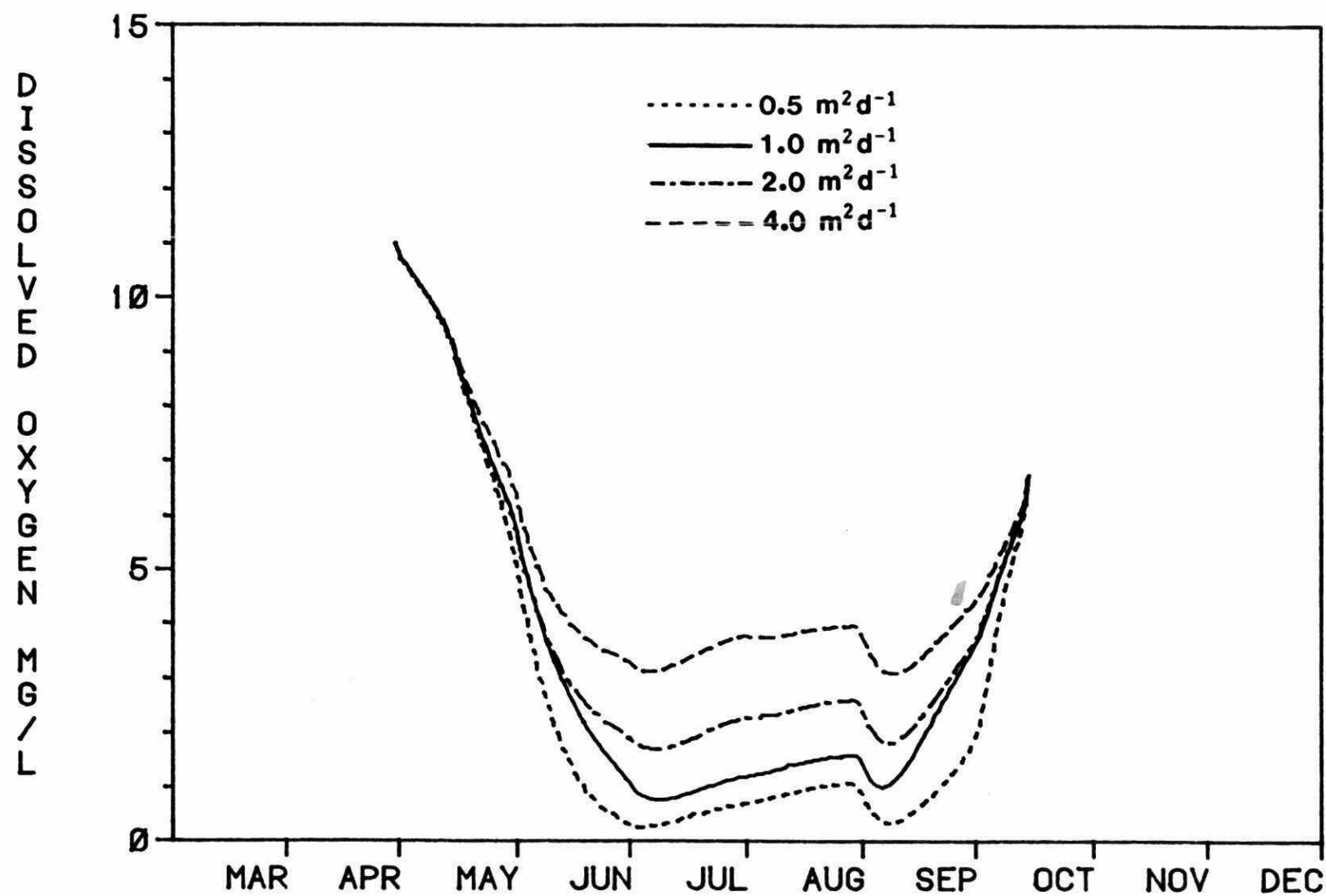


FIG. 7B. EFFECT OF VERTICAL DIFFUSION ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

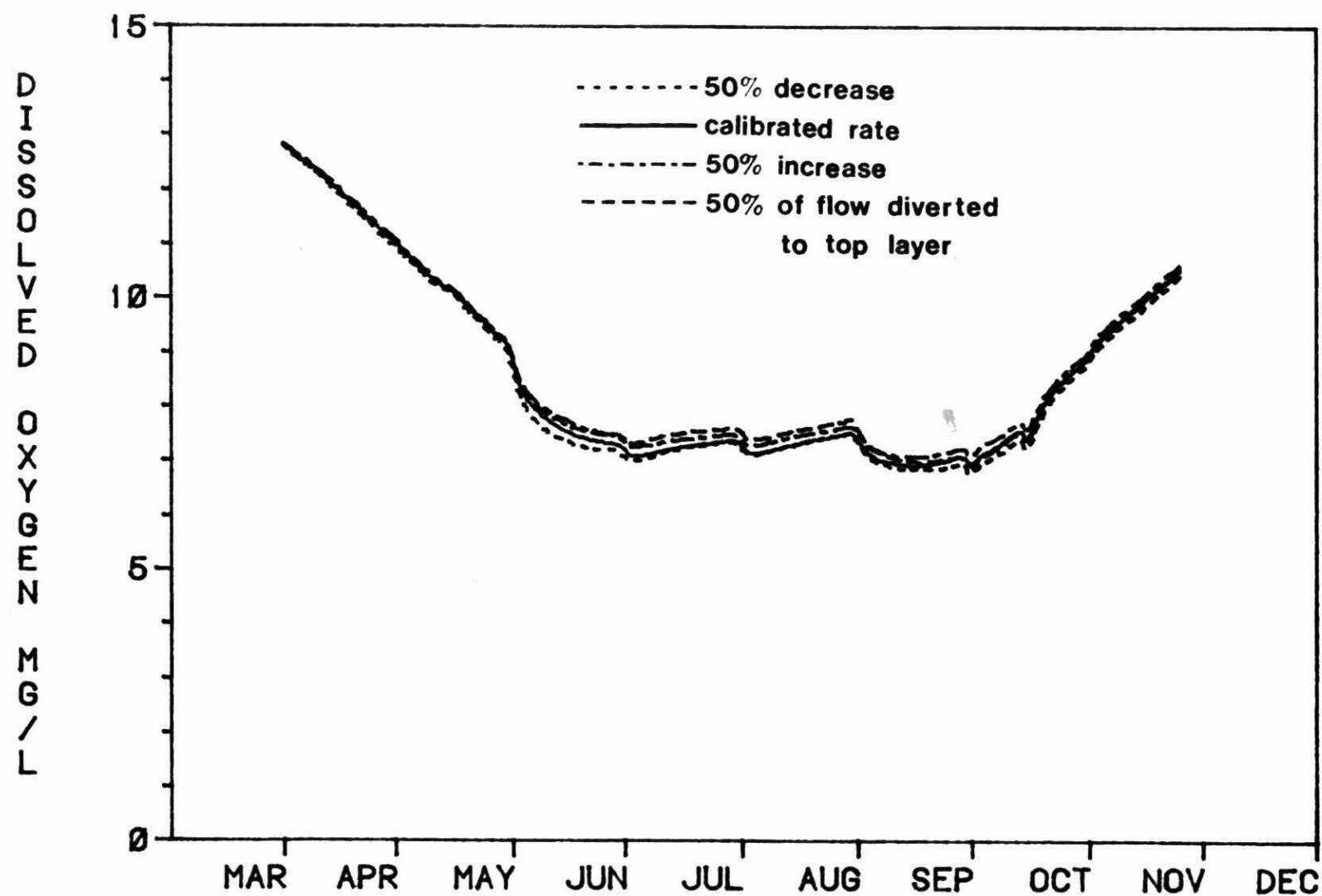


FIG. 8A. EFFECT OF LAKE-HARBOUR EXCHANGE ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.

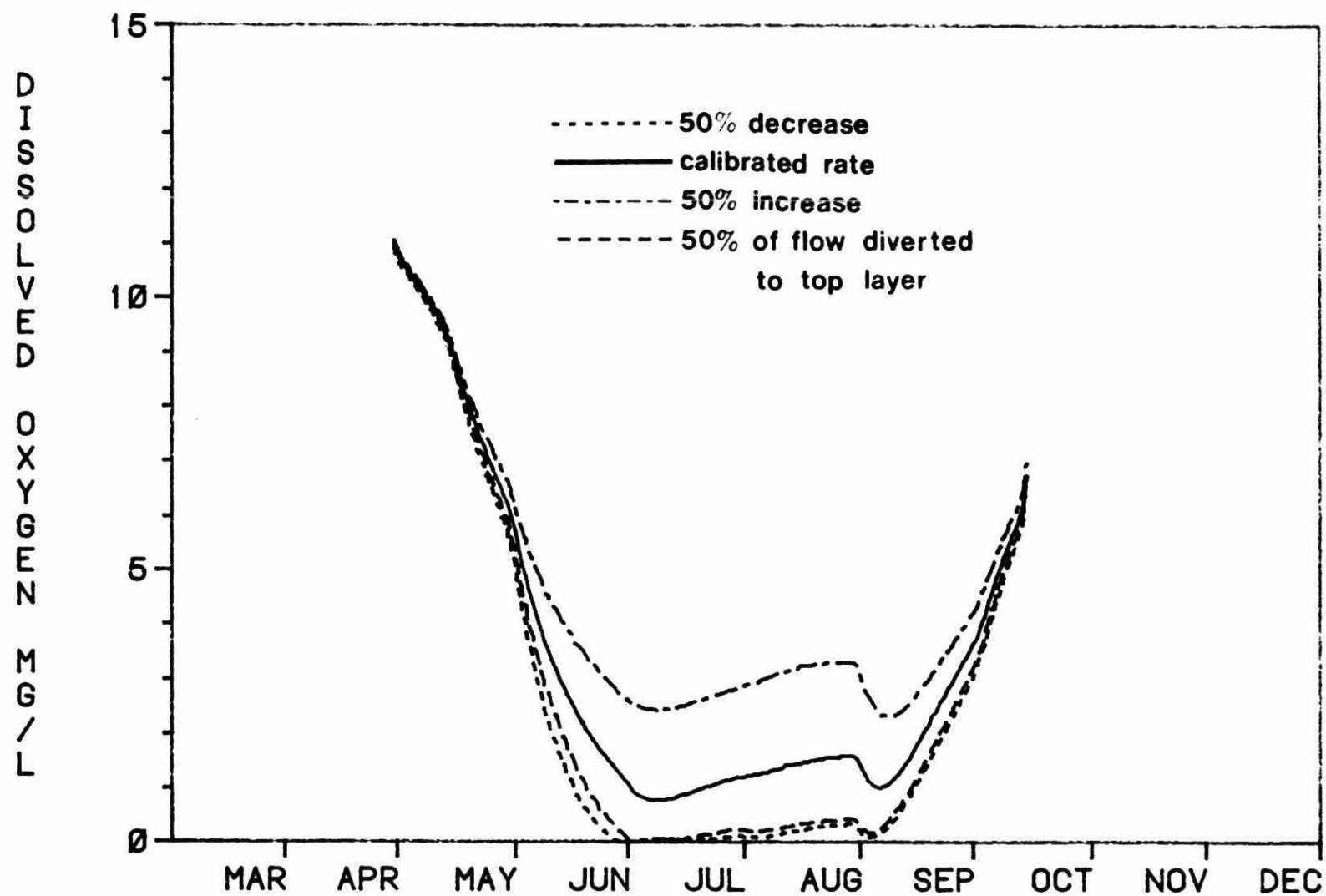


FIG. 8B. EFFECT OF LAKE-HARBOUR EXCHANGE ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

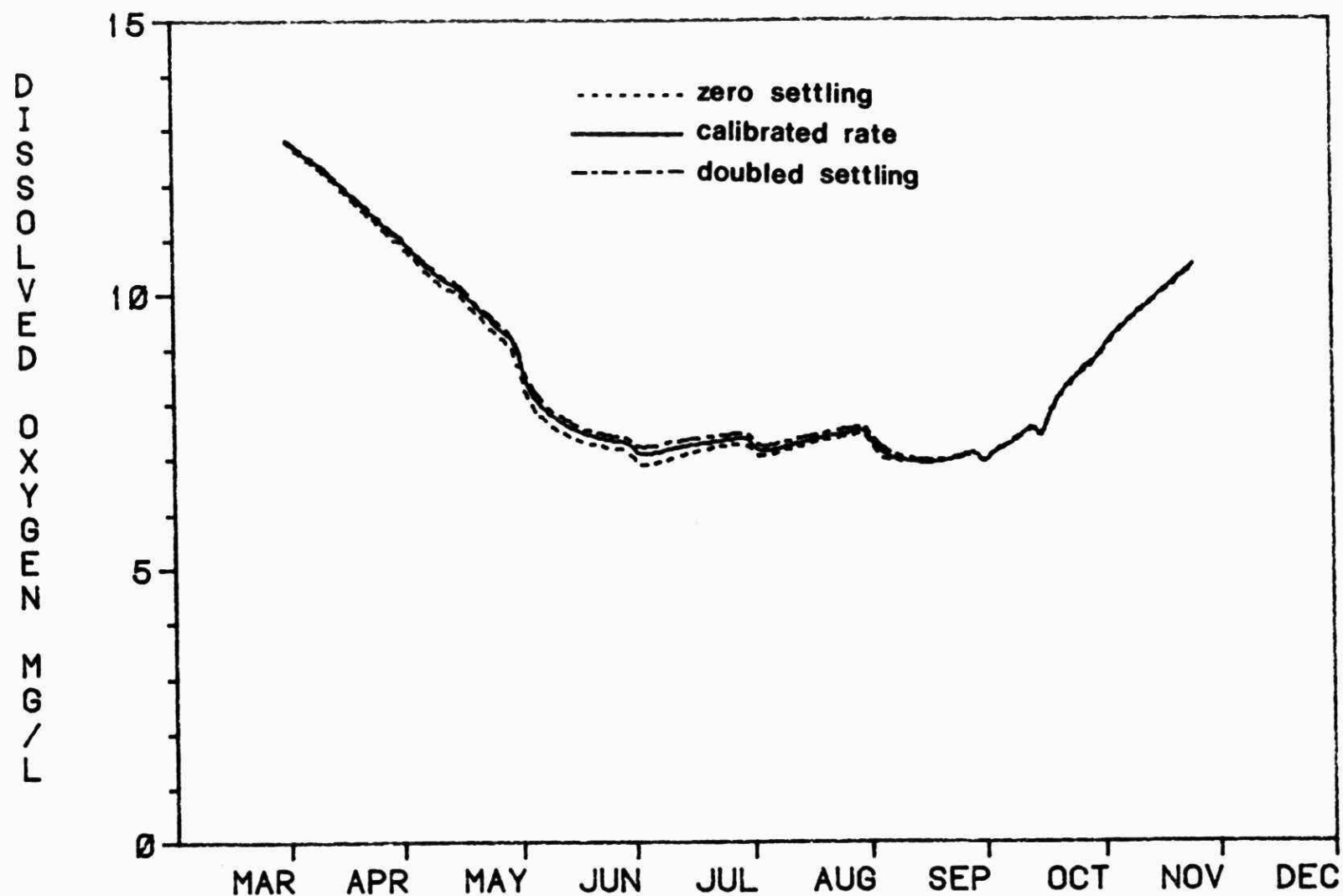


FIG. 9A. EFFECT OF VERTICAL SETTLING RATE ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.



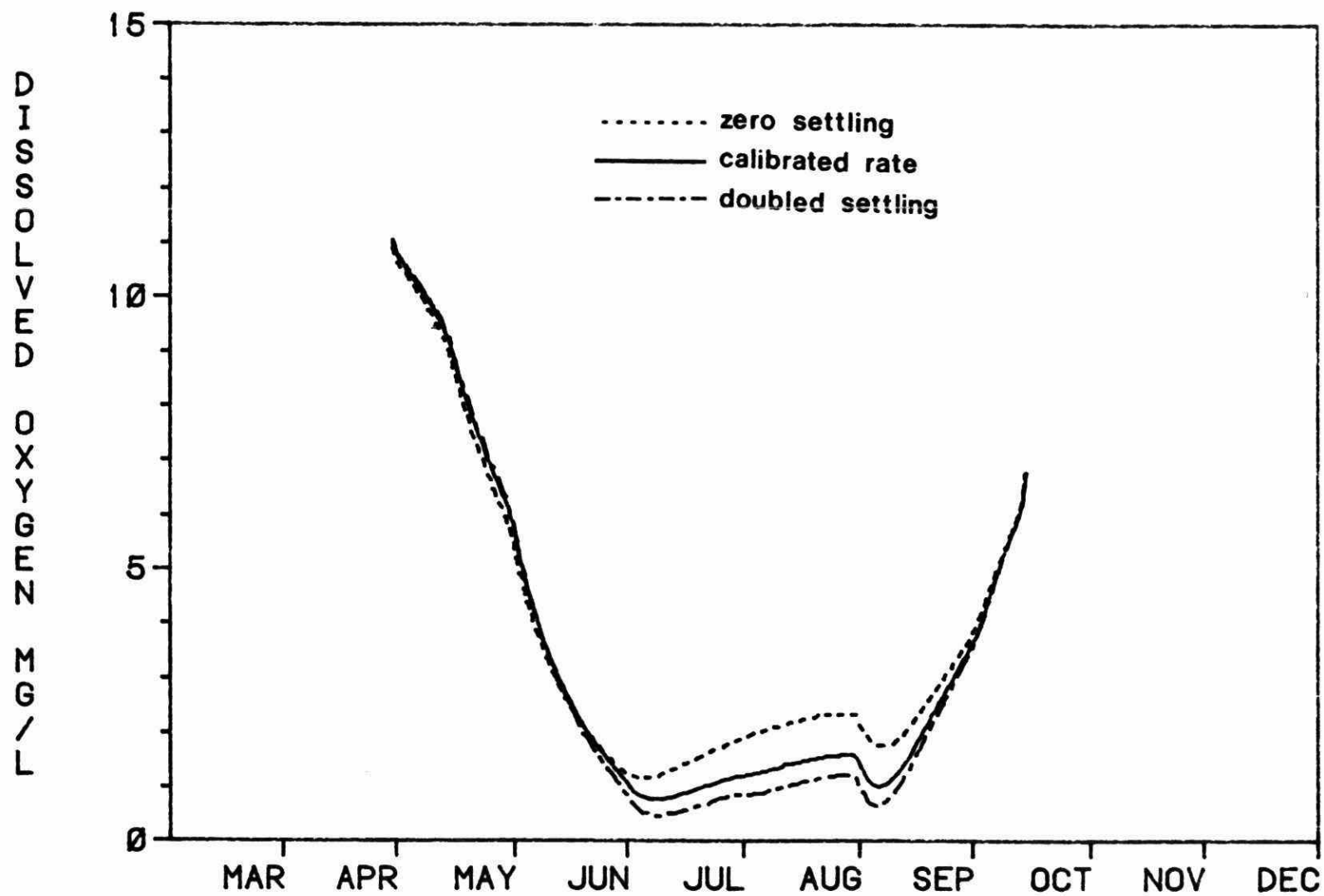


FIG. 9B. EFFECT OF VERTICAL SETTLING RATE ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

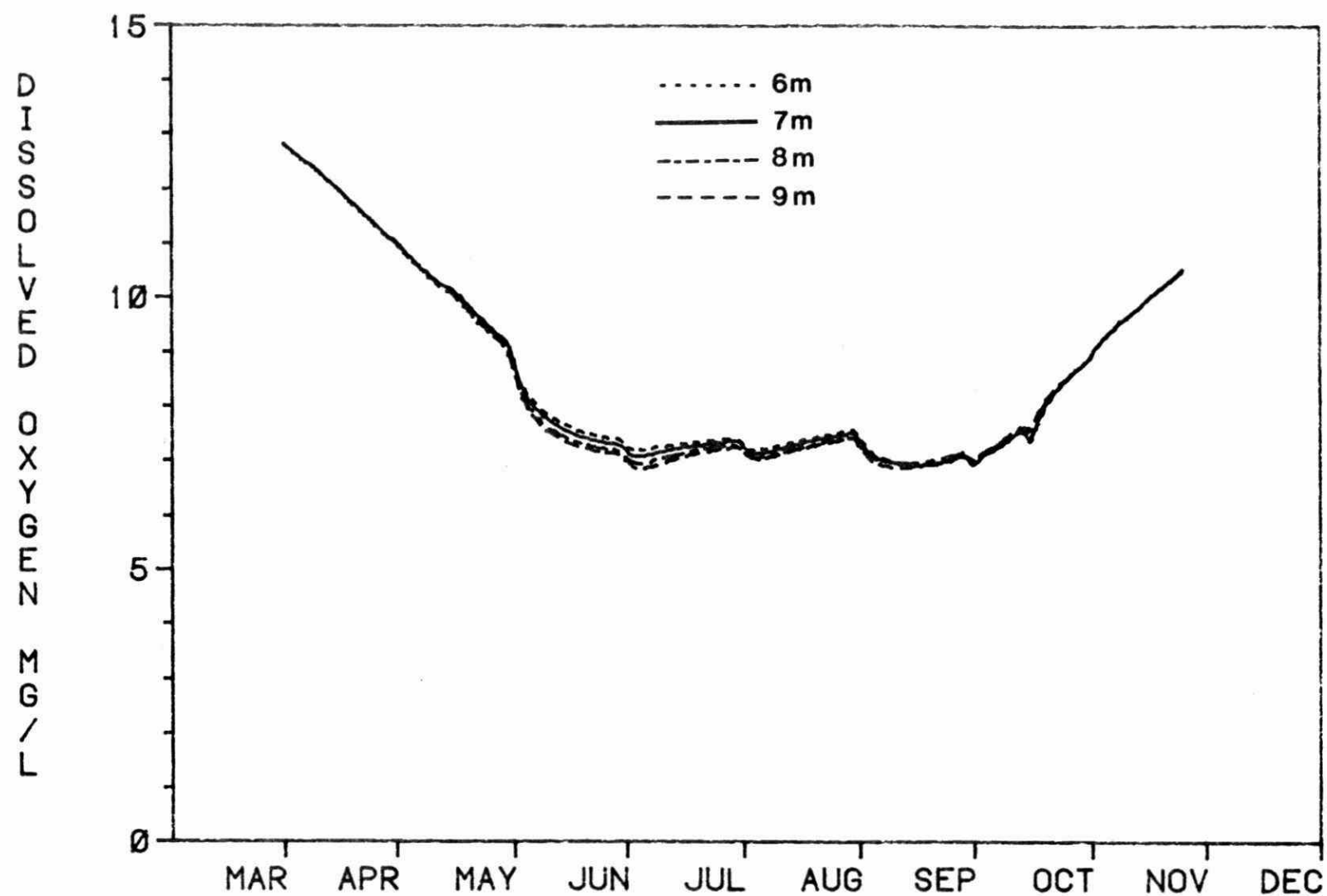


FIG. 10A. EFFECT OF STRATIFICATION DEPTH ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.

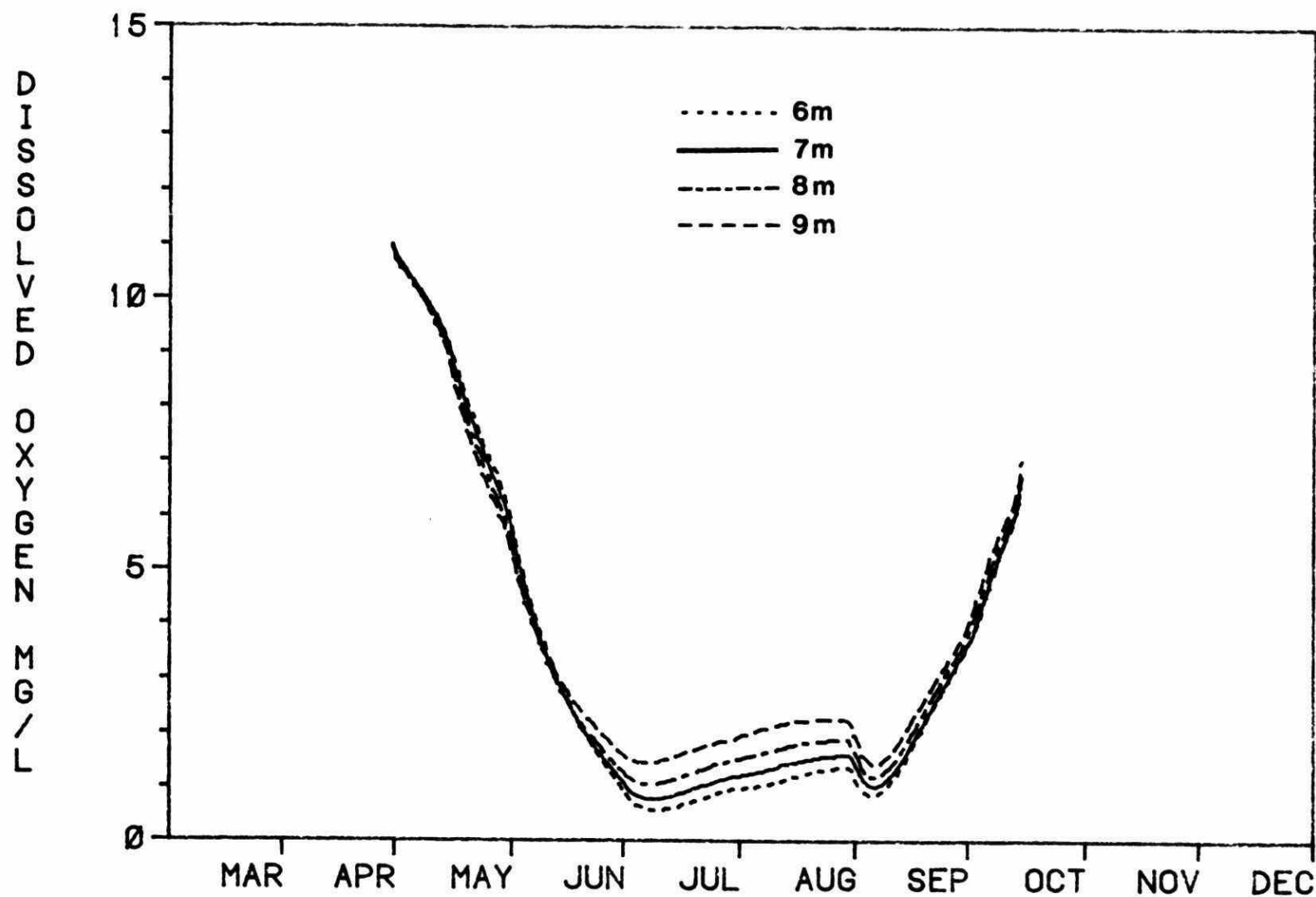


FIG. 10B. EFFECT OF STRATIFICATION DEPTH ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

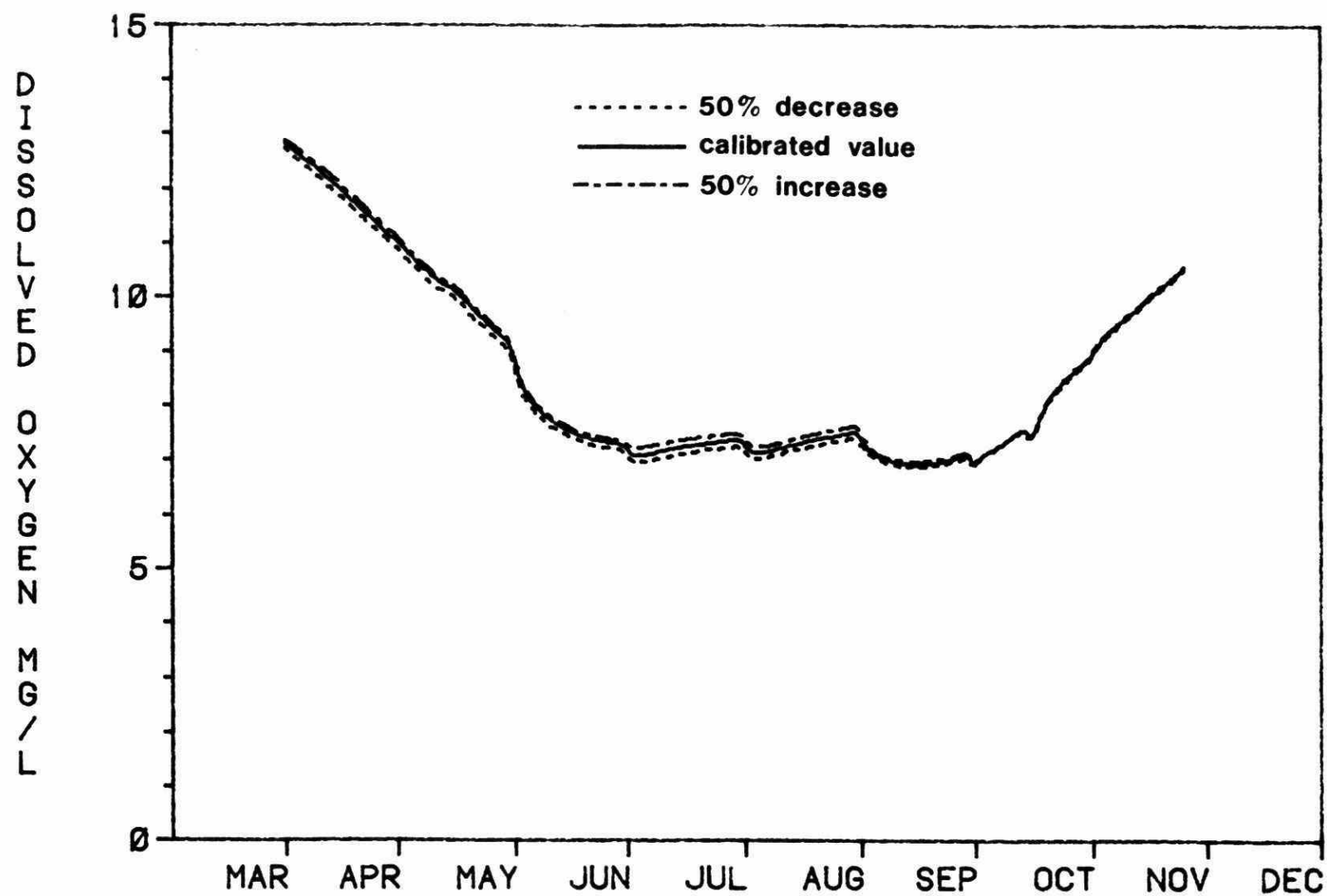


FIG. 11A. EFFECT OF PHOTOSYNTHESIS RATE ON D.O. CONCENTRATION FOR THE TOP LAYER OF HAMILTON HARBOUR.

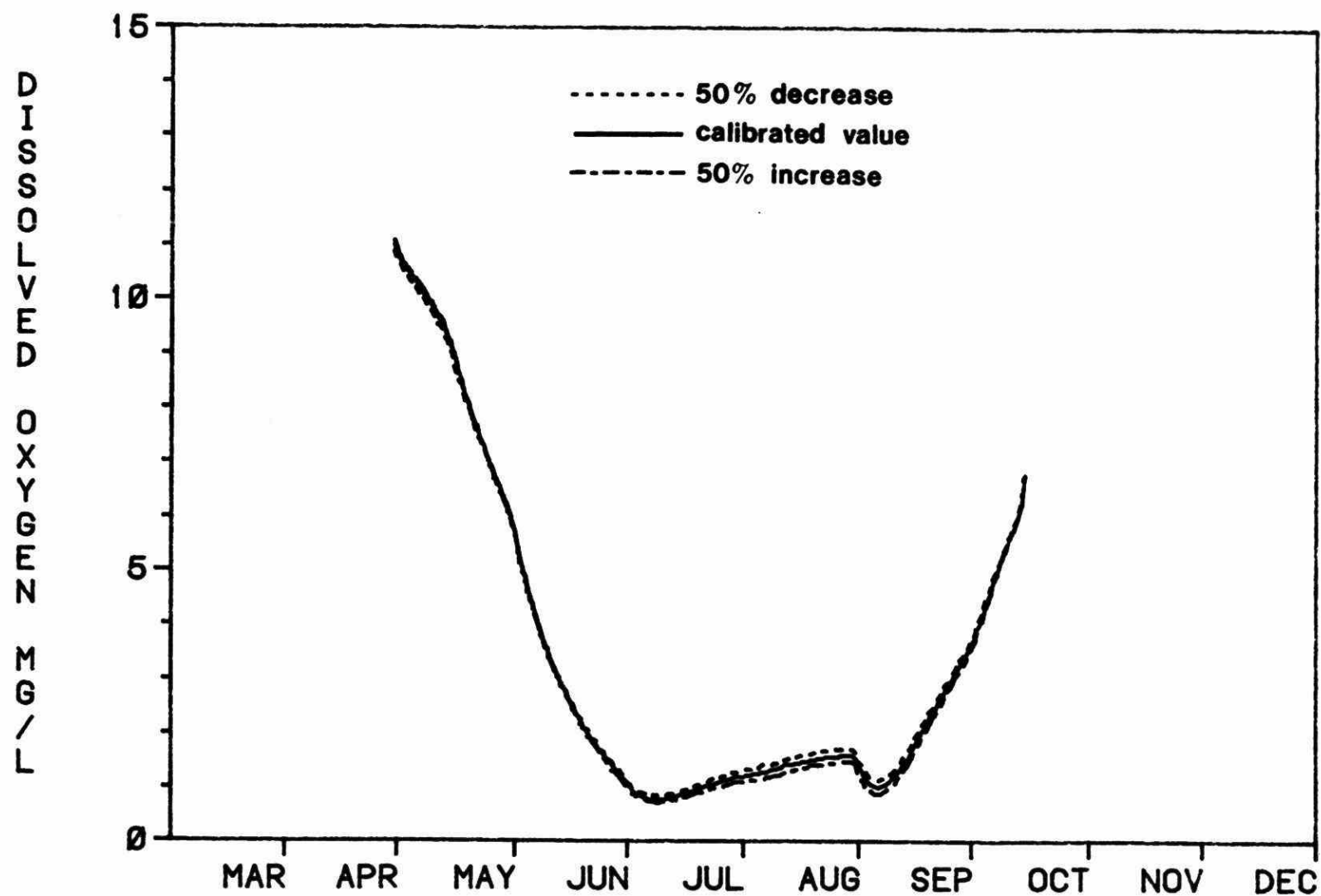


FIG. 11B. EFFECT OF PHOTOSYNTHESIS RATE ON D.O. CONCENTRATION FOR THE BOTTOM LAYER OF HAMILTON HARBOUR.

AIR POLLUTION - INDOORS, OUTDOORS, ALL AROUND THE TOWN. F. Silverman, P. Corey, S. Mintz, H.R. Hosein and P. Olver. The Gage Research Institute, 223 College Street, Toronto, Ontario.

Air pollution has been associated with adverse health effects. Difficulties in interpreting studies of health effects of exposure to air pollution arise in estimating exposure. Until recently studies of effects of air pollution have relied on pollution exposure measurements obtained from fixed location air pollution stations monitoring outside air. The assumption has been made that indoor pollution bears a fixed relationship to outdoor pollution. However substantial differences may exist between air pollution levels measured at fixed outdoor locations and actual levels inhaled by an individual, i.e. "personal" exposure. Another problem has been the use of severe symptoms or signs as sole indicators of pollution effects. Such studies would ignore minor fluctuations in disease in, for example, a group of patients with pre-existing lung disease. The definition of health status of the study group has also been uncertain in at least some reports. The present study was undertaken to address some of these problems.

Health effects of air pollution were examined in two groups of people. Both a carefully characterized group of persons with asthma and a healthy non-asthmatic control group were included. Asthmatics were chosen as study subjects because previous evidence suggested they might be more sensitive to adverse effects of inhaling air pollution. Since one of the characteristics of asthma is irritable airways, it might be expected that asthmatics would have altered sensitivity to respiratory irritant air pollutants.

The objectives of these studies are:

- 1) to estimate human exposure to air pollution by measuring air pollution levels from a) a fixed location air pollution monitoring network station, b) indoor air pollution monitoring, c) outdoor air pollution monitoring and d) "personal" air pollution monitoring;
- 2) to measure the interrelationships of these estimates of exposure.
- 3) to assess the relative strength of each of these four estimates of exposure as demonstrated by its association with health effects.

Effects of air pollution were assessed by symptom, medication and activities diaries as well as simple tests of lung function. Air pollution exposure was measured using a small portable sampler for NO<sub>2</sub>, SO<sub>2</sub> and

particulate matter; these samplers were carried by the subject ("personal") and were situated inside and outside the homes. Levels obtained were compared to data obtained from the same type of sampler located at a downtown ambient air quality monitoring station. A survey was made of house and relevant lifestyle characteristics of the volunteers and a daily record was kept of other substances to which the subjects might have been exposed.

This report used analyses of data from these studies to show that the pollutant levels were low and that there were differences between the 4 estimates of exposure. Some of the variability might be interpreted in terms of home and lifestyle characteristics of the subjects and perhaps season of the year. The intercorrelation of the pollutant levels among the 4 estimates were relatively weak. The use of such data in health studies was illustrated with examples of the lung function test results in this group of volunteers. Preliminary results of parts of this work have been reported elsewhere (1-4).

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An Assessment of Environmental Fate and Hazards  
of  
Toxic Substances

Donald Mackay

University of Toronto

Ministry of the Environment Technology Transfer Conference No. 3  
December 7, 1982  
at the Constellation Hotel, Toronto, Ontario

Abstract for  
Paper No. B7

When controlling toxic substances it is essential to develop an understanding of their sources and their environmental fate. Our aim should be to develop the capability of making quantitative statements about transport, reaction, and partitioning in the environment in order that toxic substance concentrations can be estimated in air, water, soil, food, etc. and toxicological inferences made that a given substance in a given location causes an "unacceptable" hazard, or at least probably presents a greater hazard than another situation, and thus ranks in higher priority for regulatory attention.

It is obvious that to make such statements about new and existing chemicals we require information on the substance's properties such as water solubility, vapour pressure, bioconcentration factor, sorption coefficients etc., since these properties control the environmental distribution between air, water, soil, sediment and biota. We also need reactivity data such as biodegradation, hydrolysis or photolysis rates since these rates control persistence in the environment. A short-lived chemical such as phenol is inherently of less concern than a persistent, non-reactive chemical such as a PCB. Further, we need to know how fast the chemical can migrate or transfer from one environmental compartment to another, e.g. soil to air, or water to fish. Finally, we have to have an appreciation of how rapidly a chemical's concentration will build up in a compartment such as a lake when emissions start, and conversely how long recovery may take if emissions are reduced.

For existing chemicals it is possible to analyse the environment (at

some expense) and obtain real concentration data. But for new chemicals this is impossible. In both cases it is desirable to devise a quantitative predictive capability to assess behaviour and concentrations.

Less obvious is how these diverse equilibrium, reaction, and transport data can be combined and synthesised by the regulator to produce an overall "behaviour profile" of the substance. Two approaches can be used. First, quickest, and now possible, is a scoring or ranking system in which an overall impression is gained about the likely hazard. Second, more difficult, but in the end more reliable, and becoming possible, is an environmental modelling system in which the properties serve as input to computer models which can predict behaviour. Our "fugacity models" are of this type and have the advantage that they can be used at various levels of complexity, even on hand-held computers, and certainly on currently available micro-computers. Print-outs of the models are available gratis.

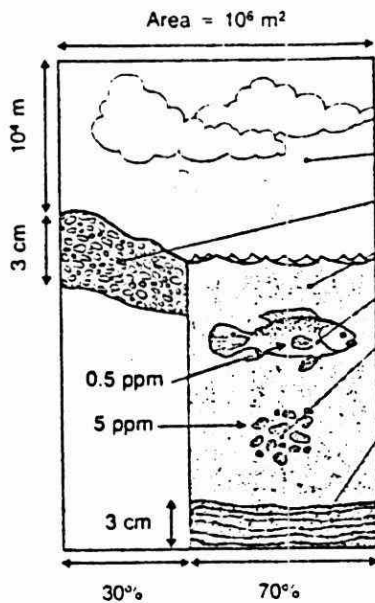
Features of the models are described and some implications discussed, particularly the next and difficult step of drawing toxicological conclusions from the model output data.

#### References

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Selected Figures attached.

FIGURE 3  
Illustrative Level I calculation



	Volume, m <sup>3</sup>	Z, mol/(m <sup>3</sup> Pa)	Amount, mol	Concentration	
				mol/m <sup>3</sup>	μg/g
Air	10 <sup>10</sup>	4.03 × 10 <sup>-4</sup>	55.0	5.50 × 10 <sup>-9</sup>	6.96 × 10 <sup>-4</sup>
Soil	9 × 10 <sup>3</sup>	1.90 × 10 <sup>1</sup>	2.33	2.59 × 10 <sup>-4</sup>	2.59 × 10 <sup>-2</sup>
Water	7 × 10 <sup>6</sup>	0.333	31.8	4.54 × 10 <sup>-6</sup>	6.82 × 10 <sup>-4</sup>
Biota	3.5	62.8	0.003	8.56 × 10 <sup>-4</sup>	1.28 × 10 <sup>-1</sup>
Suspended solids	35	37.9	0.018	5.17 × 10 <sup>-4</sup>	5.17 × 10 <sup>-2</sup>
Sediment	2.1 × 10 <sup>4</sup>	37.9	10.9	5.17 × 10 <sup>-4</sup>	5.17 × 10 <sup>-2</sup>
			100.0		

Fugacity = 1.363 × 10<sup>-5</sup> Pa

Temperature = 25 °C

Media densities (kg/m<sup>3</sup>):

Air = 1.19

Soil = 1500

Water = 1000

Biota = 1000

Suspended solids = 1500

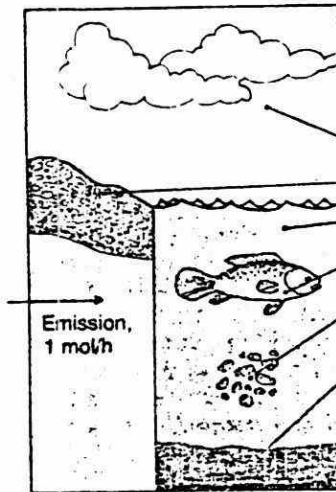
Sediment = 1500

Organic carbon contents:

Soil = 2% Suspended solids = 4%

Sediment = 4%

FIGURE 4  
Illustrative Level II calculation  
with no advection

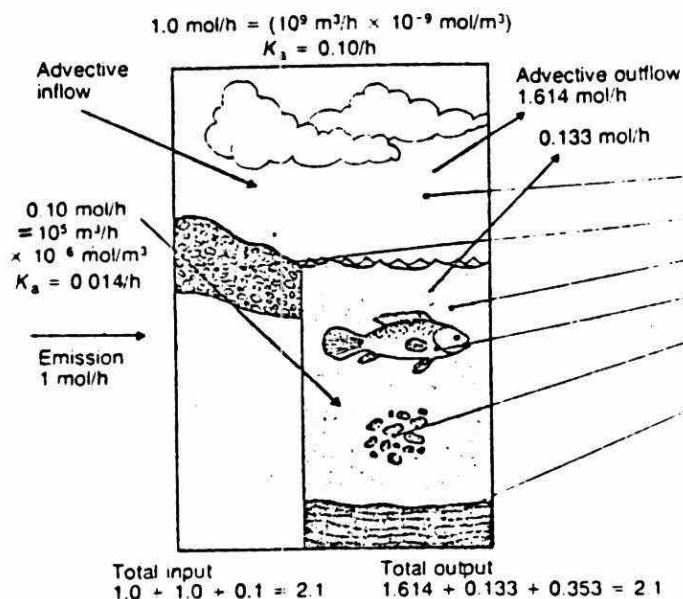


	Amount, mol	Concentration, mol/m <sup>3</sup>	Reaction, mol/h
Air	45.61	4.56 × 10 <sup>-9</sup>	0.502
Soil	1.93	2.15 × 10 <sup>-4</sup>	0.031
Water	26.38	3.77 × 10 <sup>-6</sup>	0.422
Biota	0.0025	7.10 × 10 <sup>-4</sup>	0.0002
Suspended solids	0.0150	4.29 × 10 <sup>-4</sup>	0
Sediment	9.01	4.29 × 10 <sup>-4</sup>	0.045
	82.95		1.000

Fugacity = 1.131 × 10<sup>-5</sup> Pa

Persistence = 82.95 h

FIGURE 5  
Illustrative Level II calculation with advection



	Amount, mol	Concentration, mol/m <sup>3</sup>	Reaction, mol/h
Air	16.13	1.61 × 10 <sup>-9</sup>	0.177
Soil	0.68	7.59 × 10 <sup>-5</sup>	0.011
Water	9.33	1.33 × 10 <sup>-6</sup>	0.149
Biota	0.00088	2.5 × 10 <sup>-4</sup>	8.7 × 10 <sup>-5</sup>
Suspended solids	0.0053	1.52 × 10 <sup>-4</sup>	0
Sediment	3.18	1.52 × 10 <sup>-4</sup>	0.016
	29.34		0.353

Fugacity = 4.00 × 10<sup>-5</sup> Pa

Reaction persistence = 29.34/0.353 = 83 h

Residence time = 29.34/2.1 = 14 h

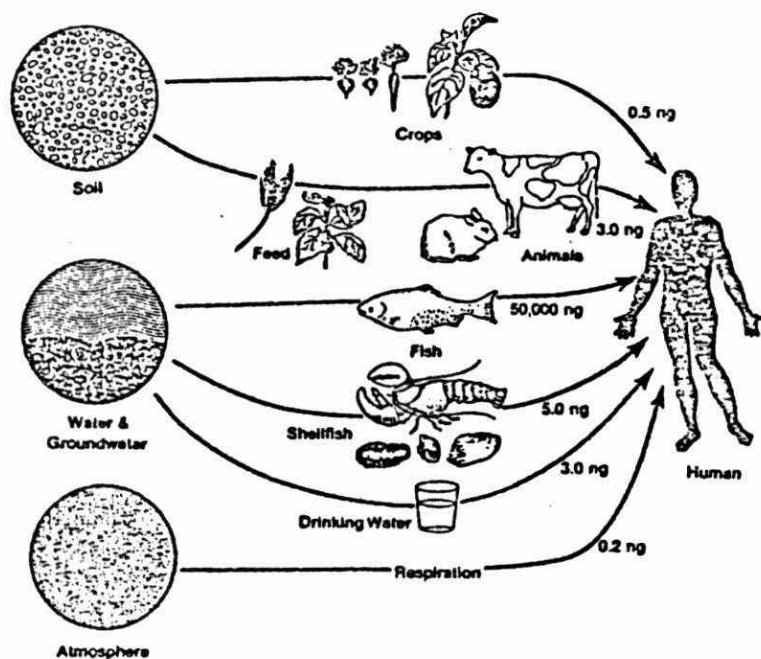


Figure 5. Pathways of Micropollutants to Humans. by Food, Drink and Respiration

**Portable Micro-Computer Program for Modelling  
Toxic Gas Dispersion in Emergencies**

Storage, handling and transportation of hazardous gases are necessary because of their extensive use in our industrial society. Toxic gases such as ammonia, chlorine and hydrogen sulfide are stored in refrigerated vessels or pressurized tanks and are transported by ship, truck, or train.

The manufacturers and shippers of these materials do their best to ensure that the materials are stored and moved safely and that hazards due to toxic properties of these materials are minimized. A great variety of failure mechanisms, however, can sometimes disrupt our lives. Those of us living in Toronto and Mississauga may remember the train derailment in 1979. A quarter of a million people were evacuated and police, firefighters, meteorologists, hospital staff, ambulance crews, and environmental scientists all played critical roles. In other countries lives have been lost in such accidents.

In 1980, computer models to calculate the estimated concentration of toxic gases in unusual releases to the atmosphere were developed by JAE Consultants as a contract program for the Ontario Ministry of the Environment. These models were developed on an IBM mainframe and they were to be used by the appropriate authorities to help them in decision making about evacuation of people in the general area of the accident. When major emergencies occur at unusual hours (as often happens), these programs can be run on a terminal at home via telephone line. If the user requires his phone line to run these models, however, his communication line is cut off. If the mainframe is down for maintenance or for some other reason, these models cannot be used.

To avoid such situations, the Ministry of the Environment adapted one of these models to a portable computer (Osborne 1). This program also contains useful information on a number of

chemicals which might be involved in crashes in Ontario. The portable computer can be brought to the crash site and used there. If kept in the homes of personnel on a rota basis, it can also be used to provide a fast information response when major emergencies occur at unusual hours.

Other models which require more input parameters and produce accurate predictions are being converted and they will be merged into the existing program on the portable computer. These programs are designed for a person having a minimum of computer competency. The more extensive models are planned to be completed by the end of 1982.

DC/mb/AR26-8

Ministry of the Environment  
Technology Transfer Conference No. 3  
December 7, 1982  
Constellation Hotel, Toronto, Ontario

Abstract for Paper B9

Development of a Combined Aerosol Impactor/Electrothermal Atomizer for  
Real-Time Environmental Analysis

J. B. French, Institute for Aerospace Studies, University of Toronto

The above device has been combined with a novel induction-coupled plasma/mass spectrometer to form a new system for multi-element analysis. This ETA/ICP/MS system has been tested on heavy metals, transition elements and rare earths, and demonstrates nanogram/ml detectability limits, multi-element response, wide dynamic range, and isotopic ratio determination capability. The many facets of the technology transfer process by which this university research has resulted in a commercial project marketed in Ontario will be described.

Summary

Development of a Combined Aerosol Impactor/Electrothermal Atomizer for  
Real-Time Environmental Analysis

J. B. French, Institute for Aerospace Studies, University of Toronto

This paper covers the technical development to date of the above device, which can provide prompt, sensitive elemental composition analysis of airborne particulates when used as a front end for an appropriate analyser.

The paper describes how this program with the Air Resources Branch, M.O.E. fits into a larger technology transfer picture in which both basic and applied work at the University of Toronto Aerospace Institute laboratories has resulted in commercial products sold internationally by SCIEX Division of M.D.S. in Thornhill, Ontario. This overall program recently resulted in the development of a prototype induction-coupled plasma/mass spectrometer system (ICP/MS) which demonstrates multi-element capability at sensitivity levels beyond those generally obtainable with more conventional ICP/atomic emission optical spectroscopy systems commercially available. The paper describes the system and includes results for many of the heavy metals, transition elements and rare earths which are of environmental concern, illustrating that picogram detectability (or equivalently, nanogram/ml of sample water) is achieved. The combination of spectral simplicity and freedom from matrix effects in the ICP is discussed in terms of improved quantification and widened dynamic range. Isotopic ratio determinations are shown (with lead as an example) which open up the possibilities of pollutant source identification. Finally, the functioning of the ETA/ICP/MS combination is described, together with preliminary results.



STANDARD AIR SAMPLERS  
VERSUS  
DICHOTOMOUS SAMPLERS  
FOR MEASURING INHALABLE PARTICULATES

JOHN HICKS AND DENIS CORR

REPORT # ARB - 48 - 82 - ARSP

# ABSTRACT

Atmospheric particulate matter collected by a number of different samplers at a central Toronto location was gravimetrically and elementally analyzed. The three different samplers used were the hivolume sampler (hivol), the size selective inlet hivol, and the dichotomous size fractionating sampler. The accumulated data were used to come to some conclusions on the operational efficiency of each sampler, its ability to predict so called inhalable particulate concentrations, and the applicability of the sample to elemental analysis.

Not only did the dichotomous sampler accurately measure particles less than 15 microns in diameter but it also size fractionated the aerosol providing some information on the degree of respiratory hazard and the source of the pollution.

## INTRODUCTION

This research was conducted through the co-operation of the Air Resources Branch, the Central Region Technical Support Group, and the Laboratory Services Branch.

The Ministry of the Environment has evaluated "inhalable particulate" sampling and assessed the performance of three particulate samplers for this task. The standard hivolume sampler (hi vol), the hivol retrofitted with size selective inlet, and the size fractionating dichotomous aerosol sampler were operated at a central Toronto location from May, 1980 to July 1982.

Research had found the hivol, which is in standard use throughout Ontario, to be inconsistent in particle collection. Variations in windspeed and direction are responsible for differing collection efficiencies of large particles. Also a sulphate artifact is present when glass fibre filters were used, thereby significantly increasing apparent atmospheric sulphate concentrations.

Results from the samplers were statistically analyzed to assess a more practical sampling methodology for measuring the respiratory hazard of particulate pollution.

An overview of particle deposition characteristics is necessary to understand the significance of measuring inhalable particulate

## LUNG DYNAMICS

Mechanisms in the respiratory passages filter and cleanse the air of particles which are inhaled through the mouth or nose. Different sized particles deposit in different parts of the respiratory tract. Airborne particles are removed by:

- 1) inertial impaction
- 2) filtration
- 3) gravitational settling
- 4) Brownian diffusion to bronchial walls and
- 5) condensation and coagulation

These deposition mechanisms operate due to the presence of tubing curvatures, nasal hairs, branching of passages and an ever decreasing diameter within the breathing passages.

The respiratory system can be broken down into 3 major sections. All have different particle size deposition characteristics, mechanisms of removal and cleansing methods. They are as follows:

### Nasopharyngeal Region (NP)

This region is made up of the nasal and oral passages and the pharynx and larynx. Deposition is facilitated by impaction on the roof and walls of the throat and nose filtration by nasal hairs. Removal of the foreign matter is by sneezing, coughing, swallowing and, in the nose, by mucociliary clearance. Mucociliary clearance is the removal of foreign matter on a thin layer of mucus which is swept along by fine constantly beating cilia. Clearance times are usually a matter of minutes. Susceptibility to ill effects is normally slight for environmental levels of contaminants except for sensitive or allergic individuals.

### Tracheobronchial Region (TB)

The tracheobronchial region is made up of a number of progressively branching passages starting at the laryngeal cavity and ending in the terminal bronchioles. The tube leading from the laryngeal cavity is called the trachea and the branches following this are called the bronchi. Close to the trachea, deposition mechanisms are facilitated by the branching and curving of the passages which promotes turbulence and impaction. The slower laminar air flow further out in this region, together with reduced bronchus diameter, promotes particle deposition by gravitational settling. Removal is by flow of mucus along the ciliated walls until deposited in the throat for ingestion. The clearance time for particles in this region is 10 minutes to 24 hrs depending on deposition site. Susceptibility to damage is greater in this region due to the longer residence times of the particles. Sensitive individuals may suffer asthma attacks due to deposition in this region.

### Pulmonary Region (P)

This region consists of the small bronchioles and alveolar clusters which form a diffusional membrane for gas transport between the bloodstream and the air. Air moves in this region is by diffusional transport and deposition usually takes place by diffusion to the walls. Removal of deposited particles is facilitated by macrophages which move the particles to the ciliated airways or lymph nodes. Clearance time of insoluble particles in this region can be months to years. Susceptibility to damage is great here due to the long residence time of particles. A relatively small mass of particulate matter is deposited in the pulmonary region because of the extremely efficient protection and clearance mechanisms of the respiratory tract.

### Size Dependence and Regional Deposition

Particle deposition studies have shown particles to deposit in the respiratory system according to their aerodynamic diameter (A.D., the corresponding diameter of a particle of unit density with the same aerodynamic characteristics)(1). As a rough approximation, particles of diameter 2.5-15  $\mu\text{m}$  deposit in the nasopharyngeal region and do little harm, particles of less than 2.5  $\mu\text{m}$  usually deposit in the tracheobronchial region and in the pulmonary region where they can do the greatest harm (see figure 1). Some of these values tend to vary depending on whether the person is mouth breathing or nose breathing, inhalation flow rate, breathing pattern, etc. A sizable fraction of the total number of inhaled particles will deposit in the respiratory system. Therefore size fractionating particulates into these size ranges gives the scientist a clearer view of the pollution danger to public health.

### Bimodal Character of Airborne Particulates

Studies of airborne particles in the environment have shown a bimodal size distribution similar to that noted in the deposition characteristics found in the lung (2). A coarse fraction  $>2.5 \mu\text{m}$  is found to be generally from natural sources caused by the breakdown of larger masses. The particles are usually generated by local sources and have a short residence time in the atmosphere due to their greater susceptibility to gravitational settling. Their chemical nature is similar to that found in crustal minerals and contain large amounts of silicon, aluminum, calcium, chloride etc.

The fine fraction is made up of particles  $<2.5 \mu\text{m}$  aerodynamic diameter and is found generally to come from man-made sources. Emissions of vapours, gas, and nuclei from industrial stacks and exhausts condense and accumulate to form sub-micron particles (3). These particles undergo coagulation into clusters

of fine particles. Their residence time in the air is longer and they can travel greater distances in airstreams than the coarse particles. The fine mode is often responsible for poor visibility on hazy days. After further coagulation they may settle, wash out or diffuse onto buildings or vegetation. Their chemical composition is made of elemental carbon, organics, metals, sulphates and nitrates.

The bimodal nature of particulates is important with respect to source, public health, residence time in the atmosphere, transport and pollution control.

### The Hivol

The standard sampler for airborne particulate monitoring in the past has been the Hivol sampler. It samples large volumes of air ( $1600 \text{ m}^3$ ) through a 8 x 10" glass fibre filter mat. Although the sampler is sturdy it has many shortcomings in its design.

The gabled roof inlet is prone to sampling biases (4). The levels of particulate measured will vary within the angle of the intake slots to the wind (fig. 2). The bias towards a certain direction becomes more pronounced as wind velocity is increased. Therefore, the sampling efficiency of the sampler will change with wind direction. In addition, the Hivol does not have a definable upper particle size cut point. The collection efficiency of large particles tends to vary with wind speed. The sampler will show an 80% sampling effectiveness for 30  $\mu\text{m}$  particles in a 2 Km/hr wind but only 40% effectiveness during 24 Km/hr winds. Therefore, the efficiency of the sampler is also dependent upon the speed of the prevailing wind (fig. 3).

The glass fibre mats are known to be high in impurities and cause sulphate artifact upon the filter (5). This artifact not only makes accurate

sulphate measurements impossible but also may be of a magnitude great enough to significantly increase T.S.P. measurements.

### The Size Selective Inlet (S.S.I.)

Hivols can be retrofitted with size selective inlet heads to remedy sampling inconsistencies caused by the original gabled roof. The round inlet shape allows unbiased sampling from any direction. Upon entering the inlet the particulates are drawn through a series of baffles which separate out particles greater than 15  $\mu\text{m}$  aerodynamic diameter on the basis of their greater settling velocity (6). Therefore, only "inhalable" particulates ( $<15 \mu\text{m}$  A.D. aerodynamic diameter) are sampled by the Hivol when the size selective inlet (S.S.I.) is attached.

The Hivol, once retrofitted with the S.S.I., is not prone to biases in wind direction, maintains an established cut point in winds of up to 25 Km/hr, and samples at close to 100% efficiency through all conditions. Sulphate artifacts are still apparent when glass fibre filters are used, however teflon coated fibre filters have been used with some success (7).

### The Dichotomous Sampler

The dichotomous sampler was modelled after inertial virtual impactors which fractionate particles according to their aerodynamic characteristics. This would simulate the behavior of the particle in the lung. Developed from the cascade centripeter, it was designed to sample only those particles less than 15  $\mu\text{m}$  aerodynamic diameter and fractionate them into the coarse (2.5 - 15  $\mu\text{m}$ ) or the fine mode ( $<2.5 \mu\text{m}$ ). The size-segregated aerosol is filtered by a chemically inert teflon membrane filter. The aerosol on the filter can be analyzed later in the laboratory.



### Inlet Head

The inlet head was designed to allow only particles smaller than 15  $\mu\text{m}$  into the sampler. Particles greater than this are too prone to gravitational settling to enter the inlet tube (8). The head is cylindrically symmetric to provide uniform sensitivity to particulates, independent of the wind direction (fig. 4). The inlet only allows particles which are capable of entering the respiratory system into the sampler. A new inlet head is available which samples particles smaller than 10  $\mu\text{m}$  but this has not yet been tested.

### Virtual Impactor

From the inlet head, the sampled particles pass through a vertical tube to the virtual impactor. The virtual impactor separates the particles into their respective coarse and fine modes. It simulates a conventional impactor in this regard but instead of an impactor plate creates a void relative to the inertial flow (9). Larger particles are carried into this void by virtue of their greater inertial momentum. Once the aerosol is aerodynamically fractionated into two air streams it is collected on teflon filters (fig. 5).

### Automation

Degree of automation is dependent upon the make of the sampler. All have programmable timing mechanisms and feedback control loops to maintain a steady pressure drop across the impactor and filters. This feedback system is essential for the maintenance of the correct size fractionation as weather conditions change or the filter resistance increases with particulate load. Some models can change samples automatically at a prespecified time or when the flow resistance of the sample is too much to maintain established fractionating cutpoints. All samplers appear to be resistant to Canadian weather conditions.

## Analysis of Samples

Loaded teflon filters were first analyzed by wavelength dispersive x-ray fluorescence spectrometry until an energy dispersive XRF unit was acquired by Laboratory Services Branch. This instrument is capable of rapidly analyzing the filters for 36 elements non-destructively. Results were compared against atomic absorption analysis of the wet ashed filters. Results of the analysis can be used for atmospheric modelling and source identification, as well as for estimating the degree of danger to public health.

## SAMPLER EVALUATION

A standard Hivol, a Size Selective Inlet Hivol and four dichotomous samplers were evaluated in a urban Toronto location. Two dichotomous samplers required manual changing of filters, while the other two were automatic. The samplers were run from October 1980 to June 1982. Each sample was taken for 24 hrs. either every 3 or 6 days depending on the sampling schedule. The sampling site 31004 on the roof of 67 College St. was used until its demise in June, 1981. The new site 31001 was constructed on the roof of Broadalbane St. Missing sampling data is due to the change in site (2 1/2 months) and various breakdowns in the different samplers.

The four dichotomous samplers evaluated were:

MODEL 3000 DICHOTOMOUS SAMPLER (VIRTUAL IMPACTOR)  
ANDERSON SAMPLERS' INC. ATLANTA' GEORGIA

SERIES 244 DICHOTOMOUS SAMPLER (VIRTUAL IMPACTOR)  
SIERRA INSTRUMENTS, CARMEL VALLEY, CALIF.

SERIES 245 AUTOMATIC DICHOTOMOUS SAMPLER (VIRTUAL IMPACTOR)  
SIERRA INSTRUMENTS, CARMEL VALLEY, CALIF.

AUTOMATED DICHOTOMOUS PARTICULATE SAMPLING SYSTEM  
BECKMAN INSTRUMENTS, FULLERTON, CALIF.

The size selective inlet head is distributed by Sierra Instruments also. "Coefficient of Haze", COH tape sampler data was obtained from MOE files for the Toronto site 31004. Although the Beckman sampler was scheduled to be operated, difficulties in maintaining regular operation made it impossible to include it in our regular sampling program. Therefore, the limited Beckman sampler data is not listed in the report.

Data analysis was accomplished using the Statistical Analysis System (SAS) utilizing the Downsvie I.B.M. computer facilities.

## DATA ANALYSIS

Statistical correlations between daily Hivol TSP measurements and Size Selective Inlet (S.S.I.) concentrations were very good ( $\text{corr.} = 0.940$ ) (see fig. 6). The collection of particulates greater than 15  $\mu\text{m}$  by the Hivol is apparent in the slope of the curve ( $m = 1.32$ ). Therefore, the measurements of the S.S.I. are always lower than those of the Hivol.

A great deal more scatter in the results ( $\text{corr.} = 0.816$ ) can be noticed in comparing Hivol concentrations vs the  $<15 \mu\text{m}$  fraction sampled by dichotomous samplers (see fig. 7). This was somewhat unexpected. When the dichotomous total is divided into fine and coarse fractions (figs. 8 and 9) the correlation with the Hivol decreased further. The correlation coefficient between the coarse fraction sampled by the dichotomous sampler and the Hivol results is 0.72. There is an even worse correlation between the Hivol and the fine fraction (0.47).

The Size Selective Inlet retrofitted Hivol (S.S.I.) correlates well with the Total Dichotomous concentrations (see fig. 10) but again, when broken down into coarse and fine dichotomous the correlation is not so good for the coarse fraction along (0.75) and worse again for the fine fraction (0.53). The ratio of the coarse to fine particulate is not static and varies daily. This is exemplified by the coarse and fine comparisons (fig 11). Therefore, although "total inhalable" particulate may be interpolated from Hivol readings by using the relation equation, coarse and fine loads cannot. Only through direct measurement with dichotomous samplers can this be achieved.

In graphically comparing samplers using glass fibre filters (Hivol and the S.S.I.) to the dichotomous total measurements on teflon filters, a y-intercept factor is always prominent. Upon closer evaluation it was possible to attribute

at least some of the y-intercept factor to the presence of sulphate artifacts on the glass fibre filters. This artifact, formed by  $\text{SO}_2$  reacting with the filter matrix, not only overestimates aerosol sulphate measurements but is also of a magnitude great enough to significantly increase TSP measurements. The inert teflon filters do not undergo any apparent reactions with the aerosol.

In figure 12 the Coefficient of Haze (COH) was compared to the dichotomous fine fraction since it was expected haze could be largely attributed to fine particles. However, only fair correlation (0.75) was found between these two measurements and one could not be estimated from the other.

Energy dispersive x-ray analysis of the dichotomous filter pairs revealed many elements to be characteristic of one particular size. Silicon, calcium, aluminum, iron and chloride are predominantly found in the coarse fractions, whereas sulphur, nickel, arsenic, lead and bromine are usually found in the fine fraction. The elements of the coarse mode are those found in crustal minerals and appear to come from larger masses which are broken down to coarse particles. In contrast, the elements of the fine mode are characteristic of those released from combustion in the form of hot gases and form nuclei upon cooling. Through the process of condensation and agglomeration these nuclei become bundles and strands of spheres which usually maintain an aerodynamic diameter of less than 2.5  $\mu\text{m}$ . It is expected that this size-dependent character can be used as a tool for source apportionment as well as calculating the rate of dispersion of the different aerosols. Although 36 elements are measured by x-ray analysis, many are of concentrations too low to warrant attention.

### Measurements Taken Throughout an Inversion Episode.

Figure 13 is a plot of the particulate concentration ( $\mu\text{g}/\text{m}^3$ ) during a pollution inversion episode in downtown Toronto. The aerosol concentrations over three days were measured by a Hivol and an dichotomous sampler. The dichotomous sampler would automatically change samples when particulate loadings became too heavy to sample consistently (i.e. pressure drops across the filters were becoming too great to maintain the 2.5  $\mu\text{m}$  cut point between fine and coarse flows). The pollution trends vary between the two samplers. For example, the Hivol shows a downward trend by Nov. 14th while in fact the fine particulate is still increasing. The fine particulate would be most injurious to those with respiratory illnesses. The greater settling velocity of the coarse particulate and the  $>15$   $\mu\text{m}$  aerosol would account for its declining concentration while the fine particles would persist in the atmosphere.

### CONCLUSIONS

1. In practice the Size Selective Inlet attachment does not seem to give a significant advantage over the Hivol, since the values measured by the S.S.I. can be adequately predicted from Hivol data.
2. The total "inhalable" particulate concentration can be approximated from Hivol measurements using a linear relation. However, the dichotomous sampler should be used to measure the coarse (2.5 - 15  $\mu\text{m}$ ) particulate matter (nasal pharyngeal deposition) and the fine ( $<2.5$   $\mu\text{m}$ ) particulate matter (bronchial and pulmonary).
3. The coefficient of haze is not an adequate measure of fine particulate.

4. A sulphate artifact on glass fibre filters is apparent which almost doubles actual values. The artifact is of a magnitude great enough to affect T.S.P. measurements.
5. Size fractionation of environmental aerosol at 2.5  $\mu$ m aerodynamic diameter not only provides the analyst with an estimation of the pulmonary and bronchial particulate deposition, but upon chemical analysis may also be used to provide relative toxicity parameters to health officials.
6. Size fractionation provides the analyst with information for source apportionment in localized settings and may be utilized in dispersion analysis of heavy pollution episodes.

#### Acknowledgements

Personnel of three separate branches of the M.O.E. should be acknowledged in this study. Of the Air Resources Branch, Dr. Robert Caton (now with Concord Scientific) and Jim J. Smith (now with Hazardous Contaminants and Standards Branch) were instrumental in the initial organization of the study. Excellent co-operation from Laboratory Services Branch was realized through the efforts of Dr. Richard Judge (now with Brock University), William Tobin, David Boomer and Dr. Brian Foster. Special thanks must be extended to the operational and technical support provided by Central Regions' Fred Austin and Danny Aquino.

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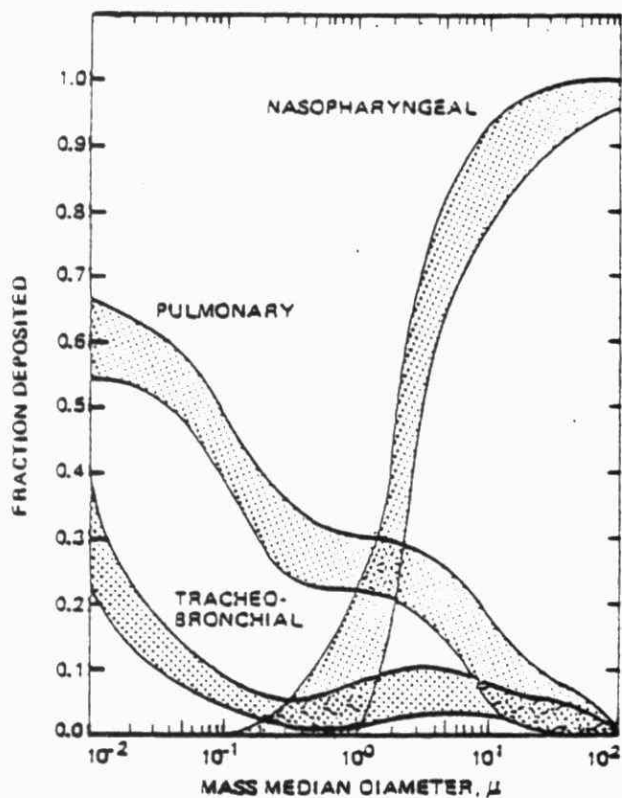


Fig. 1 Regional deposition envelopes for particle in the respiratory system. Tasks Group on Lung Dynamics, Health Phys. 12:173 (1966)

Fig. 2. The sampling effectiveness of the hivol varies with wind direction A.R. McFarland American Institute of Chemical Engineers, Houston Tx. 1979

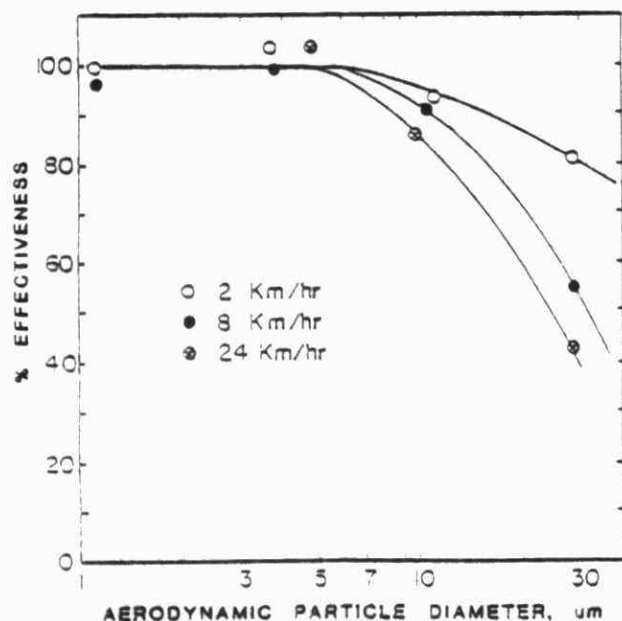
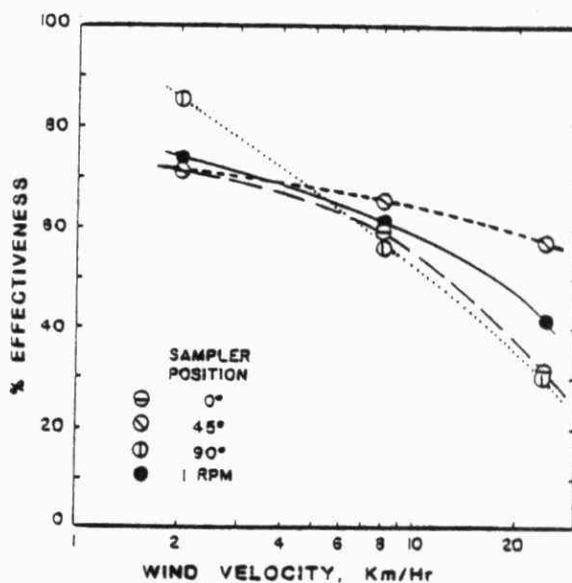


Fig. 3 The Hivol sampler does not have a defined upper size cutpoint. A.R. McFarland. American Institute of Engineers, Houston Tx. 1979.

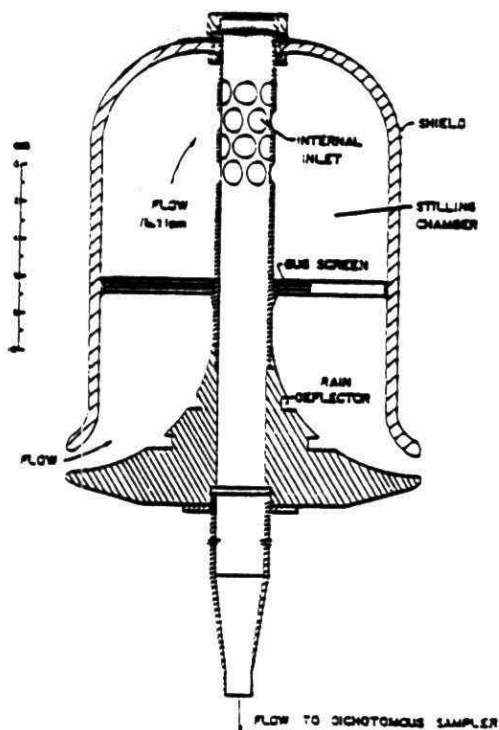


Fig. 4 Dichotomous inlet head allows only particulates less than 15 um aerodynamic diameter to enter the sampler. Wedding Env. Sci. and Tech. 14: 1367-70, Nov. 1980.

Fig. 5. Dichotomous virtual impactor assembly fractionates particulate into coarse (2.5-15 um.) and fine ( < 2.5 um) sized aerosols. Sierra 244 manual.

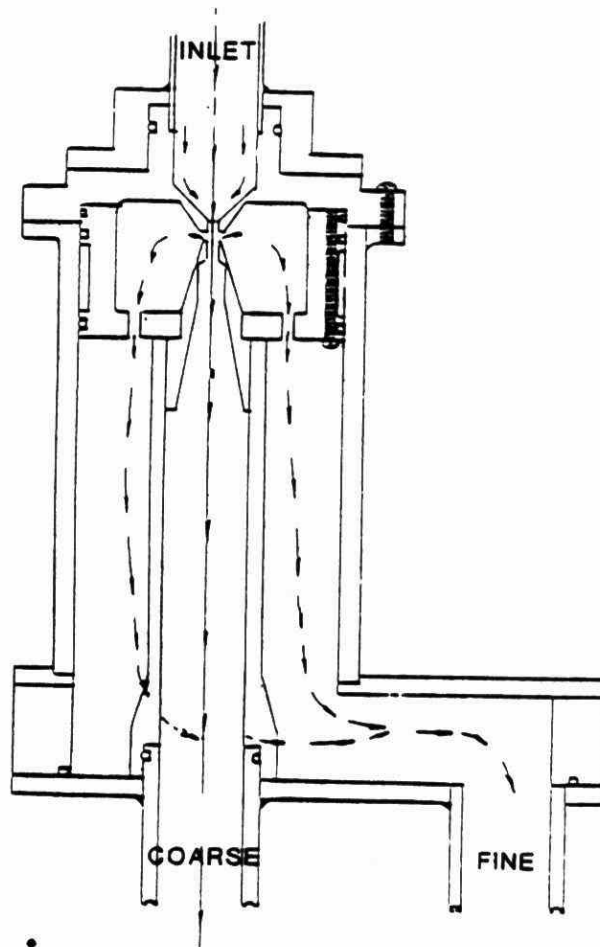


Fig 6 HIVOL VS SIZE SELECTIVE INLET HIVOL CONCENTRATIONS

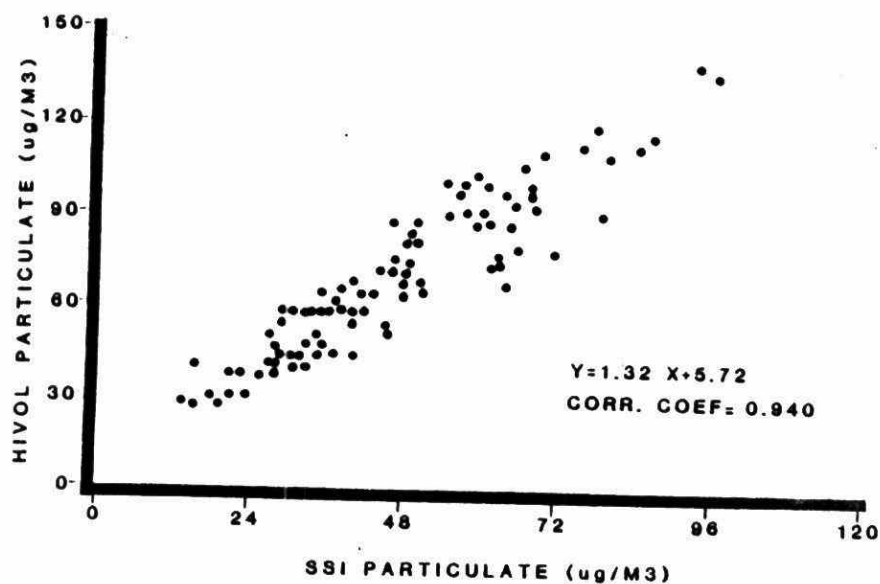


Fig 7

HIVOL VS TOTAL DICHOTOMOUS  
CONCENTRATIONS

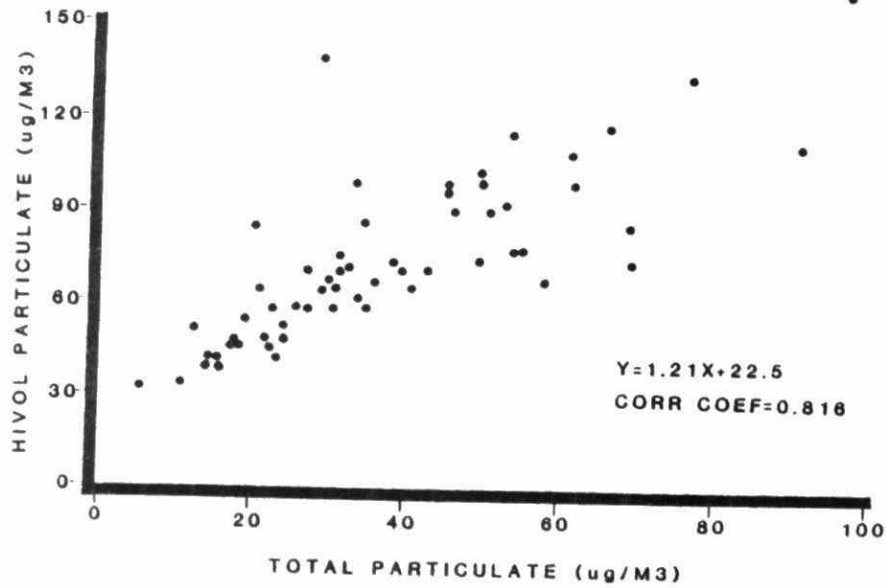


Fig 8

HIVOL VS COARSE DICHOTOMOUS  
CONCENTRATIONS

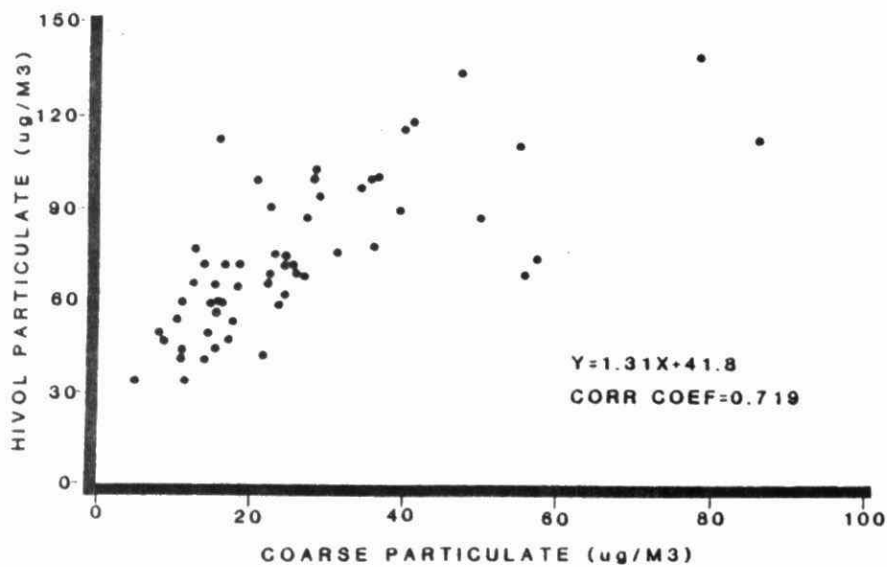


Fig 9

HIVOL VS FINE DICHOTOMOUS  
CONCENTRATIONS

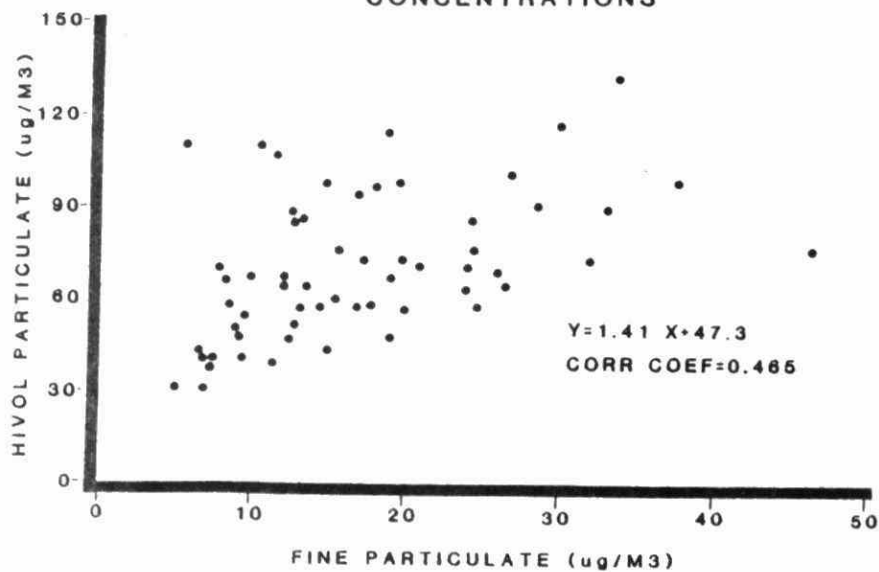


Fig 10 SIZE SELECTIVE INLET HI-VOL VS  
TOTAL DICHOTOMOUS CONCENTRATIONS

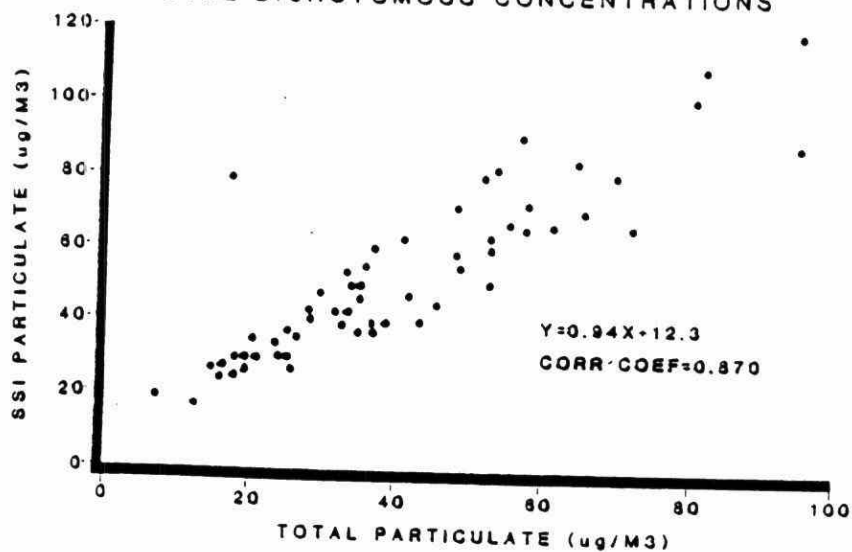


Fig 11 FINE VS COARSE DICHOTOMOUS CONCENTRATIONS

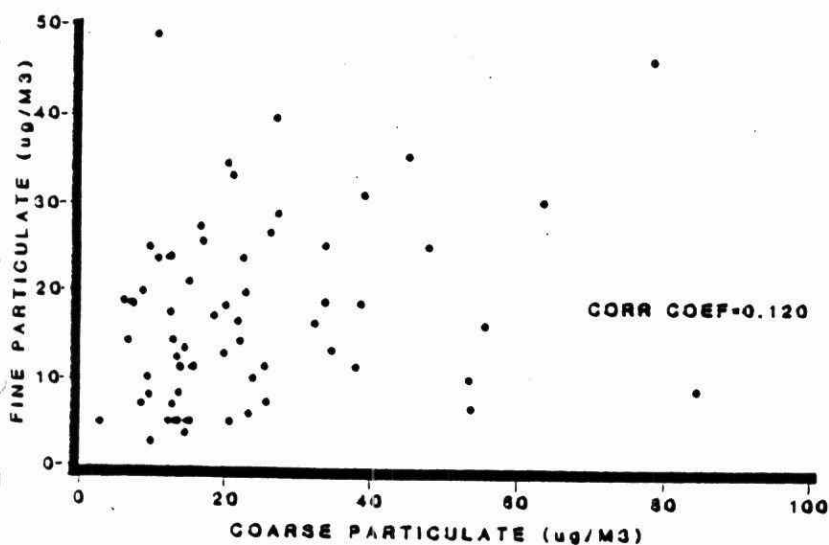


Fig 12 COEFFICIENT OF HAZE SAMPLER VS DICHOTOMOUS FINE MASS

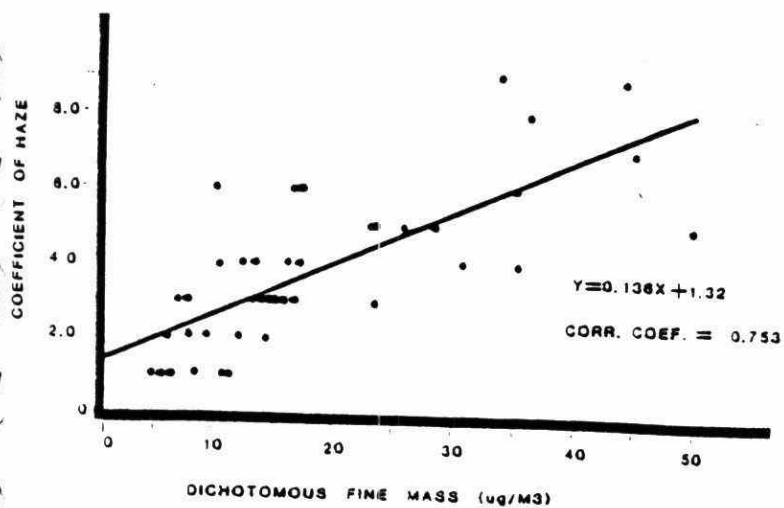
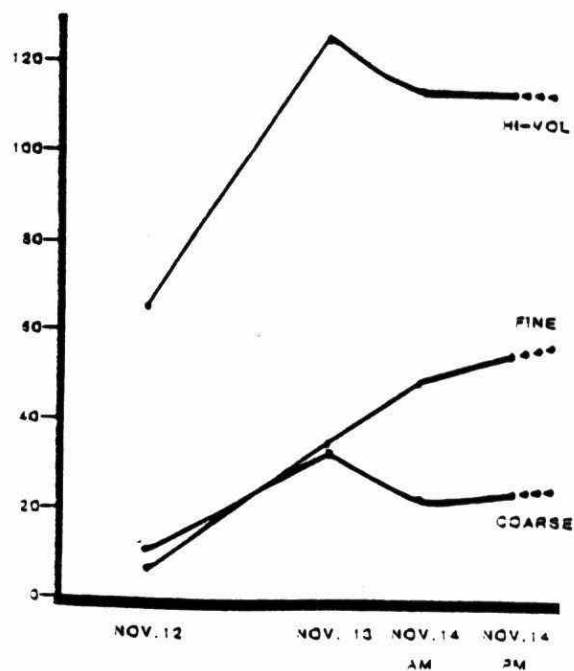


Fig 13 VARIATIONS IN PARTICULATE LEVELS DURING  
A POLLUTION INVERSION EPISODE  
IN DOWNTOWN TORONTO



REVIEW OF THE MOE RESEARCH ACTIVITIES

A Presentation to the Technology Transfer Conference No. 3  
December 7, 1982

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The mandate of the Ontario Ministry of the Environment is multidisciplinary and relies heavily on the scientific and technical information in dealing with pollution problems and the protection of the total environment and human health.

The complexity of this mandate has resulted in the Ministry opting for its issue-based strategic planning process. These issues can be identified by the Ministry's matrix-oriented Branches, Regional Offices, environmental researchers at the universities and in the private sector, with more room provided for input from public and environmental groups.

The Ministry's investment in laboratory capabilities and its numerous programs dealing with various aspects of the environment in the seventies have paid huge dividends for the characterization of ultra-traces of organic and inorganic substances of concern in air, water, soils, sediments, industrial wastes, and biota.

The recognition of the thousands of man-made chemicals and toxic metals that might enter the ecosystem is only one of the requirements which the Ontario Ministry of the Environment needs to meet the environmental challenges of the eighties. For this reason, the Ministry has reorganized its structure to face these challenges with greater confidence.

As an example, the Ministry has established, in addition to the matrix-oriented Branches, a new Branch to deal with hazardous contaminants with a major responsibility for the establishment of environmental standards and criteria, hazard and risk assessment.

This required the setting of a priority list of chemicals that might pose concern to public health and/or reflect on the quality of the total environment. This list was published by the Ministry last month.

Further effort is underway for the preparation of an inventory data-base which would include collation of the information required for the assessment process.

From this overview, the need for scientific research is necessary for the fulfillment of the aforementioned activities and for the support of the Ministry's programs. This has been demonstrated in the recent reorganization of the Ministry by the consolidation of planning, control, and dissemination of research activities through the newly established Research Coordination Office.

The roles of this unit are:

- to chair and provide support services for the Ministry's Research Advisory Committee;
- to administer the Provincial Lottery Grants and other environmental research grants such as air resources and hazardous contaminants research funds;
- to develop the Ministry's research policies and strategies;
- to monitor research performance; and
- to encourage the application of research results to the solution of environmental problems.

In May 1981, the Research Advisory Committee set up a workshop with the participation of MOE staff responsible for various areas such as air, water, waste, and abatement activities. The recommendations which emerged from that workshop were the theme

of my last year's presentation to the Second Technology Transfer Conference. They can be summarized in five major categories:

1. Isolation, identification and quantification of contaminants and their environmental effects;
2. Human health effects and the development of risk assessment;
3. Management, treatment, and containment of wastes and hazardous substances;
4. Management and treatment of drinking water, wastewater and urban run-off;
5. Transportation, deposition, and interaction of pollutants throughout the ambient environment and environmental management.

Several specific themes of research were identified under each of the above headings for 1981-82 intra and extra-mural projects as presented in Table I.

A glance at the MOE research activities in the seventies and early in the eighties demonstrates the change in research trends and objectives in spite of the fact that the goals were consistent for the protection of the environment. (See tables and histogram.) In the seventies, for example, much of the research performed was directed towards the monitoring of known chemicals, development of analytical methodologies, and the solution of specific environmental processes in water and sewage treatment plants. Additional research work evolved from the Great Lakes and Canada/Ontario Agreement programs.

Recent advances in analytical instrumentation and capabilities are having their impact on environmental research as we now can determine ultra trace quantities of contaminants and man-made



chemicals in the total environment. The reorganization of our Ministry and its dedication of a new Hazardous Contaminants Branch, as well as its efforts for the consolidation of research activities, presents a valid response to the question repeatedly asked by the public on the health effects of these contaminants.

The vast expansion of industrial activities in the seventies has resulted in huge quantities of industrial wastes. Part of these wastes have entered the environment, while the rest are being stored awaiting the development of disposal-destruction processes. Time would not be sufficient to mention other environmental issues which contribute to the challenges which our Ministry is determined to face in the 80's. As a major strategy, the Ministry has adopted an issue-oriented approach for the achievement of its goals. Once an issue is identified, the plans of the related studies would include problem definition, the factors contributing to the problem, the environmental impact and fate, the toxicity and health effects of the measured contaminants, standard setting, and the development of treatment-abatement strategy to eliminate and/or have the pollution problem under control.

A. ISOLATION, IDENTIFICATION AND QUANTIFICATION  
OF CONTAMINANTS AND HAZARDOUS CONTAMINANTS  
AND THEIR ENVIRONMENTAL EFFECTS

1. EFFECTS OF HAZARDOUS CONTAMINANTS ON THE AQUATIC ENVIRONMENT AND DETERMINATION OF SAFE AMBIENT LEVELS.
2. DEVELOPMENT OF DEVICES AND PROCEDURES FOR "CONCENTRATED" SAMPLES TO PROVIDE GREATER ACCURACY FOR AMBIENT AIR AND WATER CONTAMINANT ANALYSES.
3. DEVELOPMENT OF METHODS FOR EMERGENCY SAMPLING OF AIR POLLUTION.
4. CONTINUED DEVELOPMENT OF ANALYTICAL METHODS FOR ENVIRONMENTAL CONTAMINANTS.

B. HUMAN HEALTH EFFECTS AND THE  
DEVELOPMENT OF RISK ASSESSMENT

1. HUMAN HEALTH-EXPOSURE TO HAZARDOUS  
AIRBORNE AND WATERBORNE CONTAMINANTS  
AND DETERMINATION OF SAFE LEVELS.
2. METHODS TO DEFINE RISK OF HAZARDOUS  
SUBSTANCES TO HUMANS.
3. RAPID AND SIMPLE TEST STRATEGIES FOR  
DETECTION AND EVALUATION OF MUTAGENIC,  
TERATOGENIC AND CARCINOGENIC HAZARDS  
INCLUDING, PURE COMPOUNDS, MIXTURES AND  
ENVIRONMENTAL SAMPLES.
4. EPIDEMIOLOGICAL STUDIES TO EVALUATE THE  
IMPACT OF INDUSTRIES ON HUMAN HEALTH.

C. MANAGEMENT, TREATMENT AND CONTAINMENT  
OF WASTES AND HAZARDOUS SUBSTANCES

1. SAFETY AND FEASIBILITY OF THE LAND  
APPLICATION OF SEWAGE SLUDGE FROM A  
VIROLOGICAL STANDPOINT AND VIEWPOINT  
OF ADVERSE HEALTH EFFECTS.
2. EFFECTIVENESS OF LEACHATE COLLECTION  
SYSTEMS AT LANDFILL SITES.
3. INFILTRATION RATE THROUGH LANDFILL COVERS.
4. DEMONSTRATION OR MODELS OF NON-POINT  
POLLUTION REMEDIAL MEASURES.

D. MANAGEMENT AND TREATMENT OF DRINKING WATER,  
WASTEWATER AND URBAN RUN-OFF

1. REMOVAL OF HAZARDOUS MATERIAL FROM INDUSTRIAL AND MUNICIPAL WASTEWATERS AND SLUDGES USING EXISTING FACILITIES AND ADD-ONS.
2. REMOVAL OF HAZARDOUS MATERIALS FROM RAW WATER OR CREATED DURING TREATMENT USING EXISTING WATER TREATMENT SYSTEMS AND ADD-ON SYSTEMS.
3. IDENTIFICATION OF INDUSTRIAL MATERIALS NOT REMOVED IN MUNICIPAL WASTEWATER TREATMENT PLANTS AND DEVELOPMENT OF GUIDELINES FOR INDUSTRIAL DISCHARGES AND PRETREATMENT PROCESSES.
4. EVALUATION OF EFFICIENCY OF TREATMENT METHODS FOR THE REMOVAL OR INACTIVATION OF VIRUSES PRESENT IN RAW WATER.

E. TRANSPORTATION, DEPOSITION AND INTERACTION OF  
POLLUTANTS THROUGHOUT THE AMBIENT ENVIRONMENT  
AND ENVIRONMENTAL MANAGEMENT

1. PRACTICAL METHODS TO RECLAIM ACIDIFIED  
LAKES OR BUFFER LAKES.
2. EFFECTS ON SOIL AND VEGETATION:
  - (A) DOSE RESPONSE CRITERIA AND THRESHOLDS;
  - (B) EFFECTS OF LONG-TERM VARIABLE LEVELS;
  - (C) ACID PRECIPITATION EFFECT ON SOIL AND  
VEGETATION.
3. A STUDY OF THE CAUSE AND EFFECT ON AQUATIC SYSTEMS  
OF HIGH ALUMINUM CONCENTRATIONS IN ACIDIFIED LAKES.
4. DRY DEPOSITION DURING AIR TRANSPORT OF POLLUTANTS.